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Spectroscopic Studies On Some Group-ivb-manganese And Group-ivb-iron Metal-metal Bonds

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SPECTROSCOPIC STUDIES ON SOME GROUP IVB-MANGANESE AND GROUP IVB-IRON METAL-METAL BONDS

by

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ABSTRACT

The compounds (1) $Ph_{3-n}Cl_nGeM'$ (n = 1 or 2 and M' = $Mn(CO)_5$, or $Fe(CO)_2cp$, and (2) $Ph_{3-n}X_nSnFe(CO)Lcp$ (n = 1 to 3; X = Cl, L = CO phosphine or phosphite, and X = Br, for L = CO), have been prepared by (1) the reaction of the transition metal carbonyl anion with Ph_nGeCl_{4-n} (n = 1 or 2), and (2) by the selective cleavage of the phenyltin bond in $Ph_3SnFe(CO)cpL$ with HX, respectively. Similarly, the compounds $(C_6F_5)_nCl_{3-n}SnMn(CO)_5$ (n = 1 or 2) have been prepared by the selective cleavage by chlorine of the phenyltin bond in $Ph_{3-n}(C_6F_5)_nSnMn(CO)_5$. The reaction of $Mn_2(CO)_{10}$ or $[Fe(CO)_2cp]_2$ with the phenylchloro or phenylpentafluorophenylsilanes gives $Ph_{3-n}Cl_nSiM'$ (n = 1 or 2, and M' = $Mn(CO)_5$, or $Fe(CO)_2cp$), and $Ph_{3-n}(C_6F_5)_nSiFe(CO)_2cp$ (n = 1 or 2) respectively. The reactivity of $Ph_{3-n}Cl_nMM'$ (n = 1 to 3; M = Si, Ge, or Sn and M' = $Mn(CO)_5$, or $Fe(CO)_2cp$) towards C_6F_5 have been investigated, and is much less for M = Si.

The ^{119}Sn Mossbauer spectra of $Ph_{3-n}X_nSnM'$ (n = 0 to 3; X = Cl, Br or C_6F_5; and M' = $Mn(CO)_5$, or $Fe(CO)_2cp$), have been examined and the variation in the quadrupole splitting (Q.S.) and centre shift (C.S.) rationalised in terms of the bonding properties of the ligands around the tin. The variation in the Q.S. is dependent upon the p donor strength of the ligands and the effective symmetry of the tin nucleus, while the C.S. values are dominated by the large s character of the metal-metal bond, which increases as the more electronegative

ligands replace phenyl. The substitution of one or two carbonyl groups in the series $Ph_{3-n}Cl_nSnFe(CO)_2cp$ (n = 0 to 3) by a Group V donor ligand causes an increase in the s density at the tin nucleus, but a decrease at the iron. These changes are rationalised in terms of the σ and π bonding abilities of the ligand relative to CO.

The ^{57}Fe Mossbauer parameters of the series $X_3MFe(CO)_2cp$ (X = Ph, Cl or C_6F_5 and M = Si, Ge or Sn), show an invarient Q.S. but the small variation in the C.S. values can be explained in terms of the $-(\sigma + \pi)$ bonding abilities of the X_3M group.

From the mass spectra of $Ph_{3-n}(C_6F_5)_nMMn(CO)_5$, (n = 0 to 3; and M = Si, Ge, or Sn), $Ph_{3-n}(C_6F_5)_nMFe(CO)_2cp$ (n = 0 to 3 for M = Si, or Sn; and n = 0 and 3, for M = Ge), and Ph_3PbM' (M' = $Mn(CO)_5$, or $Fe(CO)_2cp$), the important modes of fragmentation have been elucidated by the assignment of the appropriate metastable ions. The spectra and fragmentation paths, while they show no obvious correlation with metal-metal bond strengths, are very similar for the germanium and iron derivatives but differ substantially from those of the silicon and lead derivatives. The abundances of the metal fluoride and rearrangement ions increase as M becomes heavier, and the abundances of the rearrangement ions increase for M' = $Fe(CO)_2cp$. The metal-metal bond strengths in $Ph_3SnMn(CO)_5$ and $Ph_3SnFe(CO)_2cp$ were found to be 61±8 and 54±9 Kcals/mole respectively.

The carbonyl stretching frequencies, the metal-metal stretching frequencies of some tin metal bonds, and the N.M.R. shifts of the cyclopentadienyl ring protons have been measured. From simple empirical models, the parameters cannot be readily used to determine the amount of π bonding in, or the relative strength of the metal-metal

bond.

Finally, the ^{55}Mn N.M.R. chemical shifts of $X_3MMn(CO)_5$ (X = Ph, Cl or C_6F_5; and M = Si, Ge or Sn) and $Ph_3PbMn(CO)_5$ have been shown to depend upon the ($\sigma + \pi$) bonding properties of the X_3M group while the variation in line width with the chemical shift for the series $Ph_{3-n}(C_6F_5)_nSnMn(CO)_5$ (n = 0 to 3) has been shown to depend upon the electric field gradient at the manganese atom. Both these effects are dominated by the σ-bonding properties of the organotin group.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

While the first evidence for the existence of a metal-metal bond was presented over a century ago (1), it is only in the last ten years that a large number of these compounds have been prepared and the wide scope of this field fully revealed. As a result of some imaginative preparative work, the existence of metal-metal bonds in metal carbonyls, halides, acetates, and in a variety of metal cluster compounds is now well established. Their chemistry, structure, and spectroscopic properties have been well reviewed (2-12) and have been the subject of a number of theses from this department alone. (13-16) The enormous interest in the field results from the fact that not only are these compounds of inherent interest in themselves, but they are potential catalysts (17-20) for a number of industrially important synthetic reactions and can be used as models to study the more complex metal-metal bonding systems in metals and alloys for which the more common laboratory spectroscopic techniques are not available.

It is now known that almost every metal or metalloid element in the periodic table is capable of forming metal-metal bonds and these can be divided into three classes. These are,

a) those with identical metal atoms,

e.g. Hg_2Cl_2, $Me_3SnSnMe_3$, and $(CO)_5MnMn(CO)_5$

b) those containing either two transition metal or non-transition

metal elements,

e.g. $cp(CO)_3MoMn(CO)_5$, and $Me_3SnGeMe_3$

and c) those containing a transition and non-transition metal bond,

e.g. $Me_3SnMo(CO)_3cp$, and $Cl_2GaMn(CO)_5$

It is with this last class that the majority of the chemical and spectroscopic studies have been carried out, especially on those containing a Group IV-transition metal bond, since series of those compounds can exist in which one member differs from the next by the systematic change of only one variable.

According to Lewis (5), the factors that may affect the strength of the metal-metal bond are

a) the σ effect which depends on the oxidation state of the metal and upon its electronegativity

b) the importance of any π bonding between the two metals, and

c) the possible existance of some non-bonding electronic interactions between ligands on each metal.

However attempts to gain insight into the nature of the metal-metal bond by comparison of their chemical reactivity towards attack by halogens or hydrogen halides (21-23), ethylene (24-25), phosphines or arsines (16, 23, 25), phosphites (16), sulphur dioxide (26-28), or fluorocarbons (24, 25, 29-32) have met with little success due to

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Throughout this thesis, the following symbols will be used. Ph = phenyl; Me = methyl; Et = ethyl and cp = π-cyclopentadienyl. For the sake of brevity chemical formula will be used but will be written in such a manner as to emphasise the metal-metal bond and the ligands attached to each metal. In the experimental section the compounds will be named according to the IUPAC convention,
e.g. $Ph(C_6F_5)_2SnFe(CO)_2cp$ phenylbis(pentafluorophenyl)tincyclopentadienyldicarbonyliron.

a combination of several factors. Firstly, there are too few reactions known that are common to more than one series of compounds; secondly, small changes in the molecule may cause drastic changes in the chemical reactivities; and thirdly, too few reactions have been performed on a wide enough series to allow a general rationalisation of the nature and chemical reactivity of the metal-metal bond to be made. Thus, reactions that occur with one species of metal-metal bond may give entirely different products with another or may not occur at all. Consequently, it is virtually impossible to reach any conclusions from these studies since the reaction rates, mechanisms, and reactive transition states obviously change from compound to compound. This is probably the reason why so much emphasis has been placed on the spectroscopic aspects of the metal-metal bond, since these techniques should, in theory at least, give a better understanding of the electronic distribution and strength of the metal-metal bond. These results when combined with structural and thermochemical data should give a coherent description of these molecules.

While the more common techniques of infrared (7,8,33) and proton magnetic resonance spectroscopy (7,8) have been applied to a large number of metal-metal bonded compounds, these studies are incapable of giving a very concise description of the nature or strength of the metal-metal bond, since these techniques depend on metal ligand interactions and suffer only a second order effect from the metal-metal bond itself. The only techniques available for the study of the metal-metal bond itself are Raman and low frequency infrared (7), Nuclear Quadrupole Resonance (7), Mossbauer (7,34), and the N.M.R. Spectroscopy of the metal nuclei themselves (7).

However, since with the exception of low frequency infrared and Raman spectroscopy, each of these techniques is only applicable to a few different nuclei so that predictions on other metal-metal systems are very difficult to make, since the nature of the bonding is known to change depending on the metals involved. The application of Raman spectroscopy will probably give a better indication of the metal-metal bond strength over a wide range of compounds, but such spectra are not always obtainable, and often present extensive problems in their interpretation.

Mass spectrometry has been applied (35-38) to a number of metal-metal bond systems, but the most useful information is only obtainable from the study of a series of structurally related compounds, and even so, may have little or no relationship to the electronic properties of the molecules in the ground state. This technique, however, has the advantage that it is the only practical method of determining the heats of formation of various radical species derived from the thermal cleavage of the metal-metal bond (39), and their absolute bond dissociation energies (40-45).

From the studies of the crystal and molecular structures (8-11) of metal-metal bonded compounds, the metal-metal bond distances have been accurately determined. Such bond lengths are often less than the sum of the covalent radii of the metals involved, but since these were determined from other compounds and possibly by other methods, it does not necessarily follow that the observation of a 'short' metal-metal bond is an indication of an increase in the strength or nature of the metal-metal bond, since this shortening could very well be just an indication of the error in the covalent radii used.

Only in the case of a series of structurally related compounds containing the same metals can a valid comparison be made.

The purpose of this thesis is to investigate the series of compounds $Ph_{3-n}X_nMM'$ (n = 0 to 3, X = Cl, Br or C_6F_5, M = a Group IV metal and M' = $Mn(CO)_5$ and $Fe(CO)_2cp$) by as many spectroscopic techniques as possible, from which it is hoped that some better understanding of the nature and strength of the metal-metal bond may be obtained. The discussion of the results in each of the three sections is preceeded by an introductory review of the earlier work on that topic.

CHAPTER 2

METHODS OF PREPARATION

Even though the preparation of metal-metal bonded compounds has been the subject of extensive research over the last ten years, there are only a relatively few, but by now well established successful routes to their preparation. Since these methods have been well reviewed (8-12), this section of this thesis will only be concerned with the methods used to prepare compounds described herein.

1) Reaction of a Metal Halide with a Transition-metal Carbonyl Anion in THF

This reaction is of the general type,

$$R_3MX + Na^+M'^- \xrightarrow{THF} R_3MM' + NaX$$

where R = alkyl or aryl, M = Ge, Sn or Pb, X = Cl, Br or I and M′ = $Mn(CO)_5$ or $Fe(CO)_2cp$ and is applicable to nearly all the other transition metal carbonyl anions such as $Co(CO)_4$ (46) and $Mo(CO)_3cp$ (47). This method was used to prepare $Ph_3MMn(CO)_5$ (M = Sn (23) or Ge (48, 49) and Pb (23, 48)) and $Ph_3MFe(CO)_2cp$ (M = Ge (49), Sn (23) and Pb (50)). It can also be used to prepare organohalo derivaties according to the equation,

$$R_{4-n}MX_n + Na^+M' \xrightarrow{THF} R_{4-n}X_{n-1}MM' + NaX$$

However, in this reaction the transition metal carbonyl anion is added to the organo Group IV halide so that the latter is always in excess. If this is not done or in some cases if the reaction

mixture is worked up too soon compounds containing more than one metal-metal bond may result (52). This type of reaction has been used to prepare the series $Cl_{3-n}Ph_nSnFe(CO)_2cp$ (n = 0 to 3) (51), $Ph_2ClSnMn(CO)_5$ (52) and several other tin and germanium complexes of $Co(CO)_4$ (46) and $M(CO)_3cp$ (47) (M = Mo or W).

It was also used to prepare the derivatives Ph_2ClGeM and $PhCl_2GeM'$ ($M' = Mn(CO)_5$ and $Fe(CO)_2cp$), but while the reaction of $NaMn(CO)_5$ with arylchloro germanes was simple and gave only one product, the reaction of $NaFe(CO)_2cp$ with $PhGeCl_3$ was more complicated and gave three products, $PhCl_2GeFe(CO)_2cp$, $PhGe(Cl)[Fe(CO)_2cp]_2$ and $ClFe(CO)_2cp$. At no time was the formation of $ClMn(CO)_5$ or any compound containing two metal-metal bonds formed in the reaction with $Mn(CO)_5^-$. This can be rationalised by considering the very much more nucleophilic nature (72) of $Fe(CO)_2cp^-$ compared with $Mn(CO)_5^-$, and the fact that it will tend to abstract a chlorine radical from the organometal halide to give the relatively unreactive species $ClFe(CO)_2cp$, although there may be other kinetic and thermodynamic factors involved. The electrophilic nature of the organometal halide will be expected to increase in the order $Ph_3MX > Ph_2MX_2 > PhMX_3 > MX_4$ (X = halide), but the appearance of the by-product $ClFe(CO)_2cp$ may simply reflect the number of possible sites of attack on the main group metal.

However, unlike the reaction of the tin compounds with $Fe(CO)_2cp^-$ which gave the desired metal-metal bonded compound together with some $ClFe(CO)_2cp$, analogous reaction with $PhGeCl_3$ also gave the new compound $PhGe(Cl)[Fe(CO)_2cp]_2$. This may be due to the preferential formation of a germanium iron bond at the expense of a germanium chlorine bond. It

is noteworthy that the reaction of $GeCl_4$ with $[Ni(CO)cp]_2$ (53) gives in addition to the expected products $Cl_3GeNi(CO)cp$, the compound $Cl_2Ge[Ni(CO)cp]_2$ which is in direct contrast to the analogous reaction of the tin halide, for which no bisubstituted complex was obtained.

Although this type of reaction is of fundamental importance in the preparation of tin and germanium complexes, it cannot be used for the preparation of the analogous silicon complexes except under special or forcing conditions. Thus, Me_3SiCl will react with $Fe(CO)_2cp^-$ (54) and $Fe(CO)_4^=$ (55) in THF to give the expected species $Me_3SiFe(CO)_2cp$ and $(Me_3Si)_2Fe(CO)_4$ respectively, but the analcgous reaction of Ph_3SiCl with other transition metal carbonyl anions gives none of the expected product (56). The compounds $Ph_2ClSiFe(CO)_2cp$ and $PhCl_2SiFe(CO)_2cp$ (57) have been claimed to have been prepared by the reaction of the appropriate chlorosilane with an equimolar quantity of $Fe(CO)_2cp^-$ but in low yield, and are in contrast to the reactions of silyl iodide which react smoothly with $Mn(CO)_5^-$ and $Co(CO)_4^-$ to give good yields of the silyl transition metal species (58). Although the reaction of Me_3SiCl with $NaMn(CO)_5$ in THF does not give trimethylsiliconpentacarbonylmanganese, neat Me_3SiCl readily reacts with solid dry $NaMn(CO)_5$ at room temperature to give good yields of $Me_3SiMn(CO)_5$ (59). The course of the reaction of Ph_3SiCl with various transition metal anions (56) has been found to give variable yields of hexaphenyldisiloxane $(Ph_3Si)_2O$ together with hydrido, chloro, or polynuclear transition metal species, depending on the carbonyl anion used. Only in one case, that between Ph_3SiCl and <u>trans</u> $NaCo(CO)_3PPh_3$ was any silicon transition metal species isolated. The origin of the oxygen in the disiloxane is not clear, but is thought to come from

the metal carbonyl and not the solvent. Clearly, the course of these reactions is not just dependent on the nucleophilicity of the carbonyl anion, but on other factors that are not well understood.

Very recently certain silicon transition metal bonds have been made by the reaction of various organolithio silanes and germanes with chlorotransition metal species (60),

e.g. $Ph_3MLi + Cl_2M'(cp)_2 \rightarrow Ph_3MM'(Cl)(cp)_2$

M = Si or Ge and M' = Zr or Hf

but complete replacement of both chlorines is apparently impossible.

2) Reactions of Silanes with Metal Carbonyl Dimers

This reaction is by far the most widely used for the preparation of silicon-transition metal bonds, but although it could be of considerable use for other main group transition metal bonds such reactions of main group hydrides have not been widely explored. However, the reaction of some dialkyl aluminum hydrides with $HM(CO)_2L$ (M = Mo (61) or W (62), L = CO or PPh_3) have been shown to give some aluminum transition metal species, and the reaction of Me_3SnH with $Fe(CO)_5$ (63) and of Et_3GeH with $Co_2(CO)_8$ (64) has been shown to give $(Me_3Sn)_2Fe(CO)_4$ and $Et_3GeCo(CO)_4$ respectively.

The reaction of silanes of the type X_3SiH (X = Cl, Ph etc.) with metal carbonyls and their derivatives fall into two classes. The first of these performed at moderately low temperatures and in the presence of U.V. irradiation results in the oxidative addition of the silane to the transition metal carbonyl giving a silicon transition metal carbonyl hydride and the elimination of carbon monoxide,

e.g. $cpMn(CO)_3 + HSiCl_3 \xrightarrow{h\nu} cpMn(H)(CO)_2SiCl_3 + CO$ (65)

$C_6H_6Cr(CO)_3 + HSiCl_3 \xrightarrow{h\nu} C_6H_6Cr(CO)_2(H)SiCl_3 + CO$ (65)

$Rhcp(CO)_2 + HSiPh_3 \xrightarrow{h\nu} cp(CO)Rh(H)SiCl_3 + CO$ (66)

This is thus similar to the oxidative addition of the Group IV tetrahalides to $Fe(CO)_5$ and $Co(CO)_2cp$ (67),

e.g. $MX_4 + Fe(CO)_5 \longrightarrow X_3MFe(X)(CO)_4 + CO$

(M = Ge, Sn and X = halide)

These hydrides are in fact best described as acids, and thus the compound resulting from the reaction of Cl_3SiH with $Fe(CO)_5$ will react with tertiary or quaternary amines such as $Et_4N^+Cl^-$ to give $Et_4N^+[Fe(CO)_4SiCl_3]^-$ and HCl (68).

At higher temperatures, and without U.V. irradiation a different reaction occurs giving a silicon transition metal bond and the release of hydrogen,

e.g. $2X_3SiH + Y_2 \rightarrow 2X_3SiY + H_2$

X = Cl for Y = $Mn(CO)_5$, $Fe(CO)_2cp$, $Mo(CO)_3cp$, $Ni(CO)cp$ (69) and $Co(CO)_4$ (70)

X = Ph for Y = $Mn(CO)_5$, $Re(CO)_5$ (48) and $Fe(CO)_2cp$

X = C_6F_5 for Y = $Mn(CO)_5$, $Re(CO)_5$, $Co(CO)_4$ and $Fe(CO)_2cp$ (71)

X = Me for Y = $Mn(CO)_5$, $Co(CO)_4$ (72)

The reaction of Cl_3SiH with $[Fe(CO)_2cp]_2$ is, however, more complicated resulting in the formation of the expected product $Cl_3SiFe(CO)_2cp$ and varying amounts of $(Cl_3Si)_2Fe(H)(CO)cp$, $Cl_3Si[Fe(CO)cp][Fe(CO)_3cp]$, and $[cpFe(CO)_3]^+[FeCl_4]^-$ depending upon the temperature and the mole ratio of the reactants used (73).

The general course of the reaction is thought to pass through the carbonyl metal hydride as an intermediate,

e.g. $Ph_3SiH + Mn_2(CO)_{10} \rightarrow Ph_3SiMn(CO)_5 + HMn(CO)_5$

which then reacts with more silane to give the silicon-transition metal species and hydrogen,

$$Ph_3SiH + HMn(CO)_5 \rightarrow Ph_3SiMn(CO)_5 + H_2$$

This reaction scheme is supported by the observation that Me_3SiH reacts very readily with $HCo(CO)_4$ (72) and that other strong nucleophiles, such as dialkylamides also react with transition metal hydrides, (74)

$$Me_3MNMe_2 + HM'(CO)_3cp \rightarrow Me_3MM'(CO)_3cp + HNMe_2$$

(M = Si, Ge, or Sn and M' = Cr, Mo, or W)

The preparation of $Ph_3SiFe(CO)_2cp$ and of the series $Ph_{3-n}X_nSiFe(CO)_2cp$ (n = 0 to 3 and X = Cl or C_6F_5) $Ph_{3-n}Cl_nSiMn(CO)_5$ and $(C_6F_5)_3SiMn(CO)_5$ were accomplished by the general method,

$$Ph_{3-n}X_nSiH + (M')_2 \rightarrow Ph_{3-n}X_nSiM' + H_2$$

(n = 0 to 3, X = Cl or C_6F_5 for M' = $Fe(CO)_2cp$; n = 0 to 3, X = Cl, for M' = $Mn(CO)_5$; and n = 3, X = C_6F_5 for M' = $Mn(CO)_5$) and similar to that used for the preparation of $PhCl_2SiCo(CO)_4$ (70), and $MeCl_2SiFe(CO)_2cp$ (69).

Using an excess of silane, the silicon-transition metal compound, hydrogen and unreacted silane were the main products. The yields for most reactions were between 50 and 30% but for the reactions with the solid silanes Ph_3SiH and $(C_6F_5)_3SiH$, extensive charring and decomposition of the reactants resulted in yields of less than 20%.

A few germanium-transition metal bonds have been made by a similar method but this involves the elimination of HCl from the reaction of the transition metal carbonyl halide with Cl_3GeH,

$$2Cl_3GeH + ClM' \rightarrow 2Cl_3GeM' + HCl$$

$(M' = Mn(CO)_5$ (75) and $Fe(CO)_2cp$ (70))

Identical products are formed in the reaction of the transition metal dimer with Cl_3GeH, but while the reaction with $Mn_2(CO)_{10}$ only proceeds above 100°, that of $[Fe(CO)_2cp]_2$ is spontaneous at room temperature and gives essentially a quantitative yield of $Cl_3GeFe(CO)_2cp$. This is again an indication of the very much stronger nucleophilic nature of the iron dimer with respect to the other metal carbonyls.

3. Selective Cleavage of Organo-tin bonds with Halogens or Hydrogen Halides

The reactivity of many Group IVB-transition metal bonds towards halogens or hydrogen halides can result in the cleavage of either the metal-metal or metal-carbon bond. Attack of the metal-carbonyl or metal-cyclopentadienyl bond is also possible but since this type of reaction has never been observed it is considered to be energetically unfavourable. The extent to which either of the two reactions occur is a measure of the relative reactivity of the metal-metal or metal-carbon bond and can be thought to be loosely correlated with the bond strength. It is, however, very difficult to predict the cause of any given reaction based on known or estimated bond strengths since very small changes in the ligands or the metals may produce drastic changes in the products obtained. In addition, because too few reactions common to more than one series of metal-metal bonded compounds have been studied, and no rational assessment of their chemistry has been made, it is nearly impossible to predict the cause of any given reaction, based on the reactivity of the compounds.

The great majority of reactions either result in the cleavage of the metal-metal bond,

$$Me_3MFe(CO)_2cp + Cl_2 \rightarrow Me_3MCl + ClFe(CO)_2cp$$

M = Si, Ge or Sn (14)

or in the replacement of all the organic groups about the Group IV atom,

e.g. $Ph_3MM'(CO)_5 + X_2 \rightarrow X_3MM'(CO)_5 + 3PhX$

M = Xn, X = Cl or Br, M' = Mn (23); M = Ge, X = Cl or Br, M' = Mn (78)
M = Sn, X = Br, M' = Re (48) and X = Cl, M' = Re (79)
There are consequently few reactions that result in the controlled replacement of one or two organic groups and some of these are given in Table 2-1.

It will be apparent that the majority of compounds that undergo this type of reaction are tin compounds, since the analogous germanium or silicon derivatives either fail to react, or result in cleavage of the metal-metal bond. Lead-transition metal systems have not been widely investigated but probably react by the cleavage of the metal-metal bond as in the reaction of $Ph_3PbMn(CO)_5$ with HCl or chlorine (23). Of the large number of compounds studies which contain the $Fe(CO)_2cp$ group, only $Me_3SnFe(CO)_2cp$ (14) reacts with retention of the metal-metal bond, and for the systems containing $Co(CO)_4$ all of these react by cleavage of the metal-metal bond (81). The rate determining step for these latter derivatives is probably related to their tendency to ionise in solution. (82)

Since the reaction of excess HCl with $Ph_3SnFe(CO)_2cp$ gives an almost quantitative yield of $Cl_3SnFe(CO)_2cp$ (23), the reaction of one or two moles of HCl upon one mole of $Ph_3SnFe(CO)_2cp$ should give $Ph_2ClSnFe(CO)_2cp$ and $PhCl_2SnFe(CO)_2cp$ respectively. Thus it was

Table 2-1

Selective Cleavage of the Organotin Bonds in some Group IV-Transition Metal Systems by Halogens or Hydrogen Halides

Compound	Reactant	Mole-ratio	Product	Yield %	Reference
$Ph_3SnMn(CO)_5$	HCl	excess	$PhCl_2SnMn(CO)_5$	80	23
$Ph_3SnMn(CO)_5$	Br_2	1:2	$PhBr_2SnMn(CO)_5$	85	23
$Et_3PbMn(CO)_5$	HCl	1:1	$Et_2ClPbMn(CO)_5$	90	13
$Et_3PbMn(CO)_5$	Cl_2	1:1	$Et_2ClPbMn(CO)_5$	57	21, 13
$Me_3SnMn(CO)_5$	HCl	1:1[b]	$Me_2ClSnMn(CO)_5$	71	21
$Me_3SnMn(CO)_5$	HCl	excess[c]	$MeCl_2SnMn(CO)_5$	26	21
$Me_3SnFe(CO)_2cp$	HCl	excess	$Me_2ClSnFe(CO)_2cp$	--	14
$Me_3SnMo(CO)_3cp$	HCl	excess	$Me_2ClSnMo(CO)_3cp$	90	15
$Me_3SnMo(CO)_3cp$	HCl	excess[d]	$MeCl_2Mo(CO)_3cp$	--	15
$Me_3SnW(CO)_3cp$	HCl	excess	$MeCl_2SnW(CO)_3cp$	33	15
		plus	$Me_2ClSnW(CO)_3cp$[e]	66	15
$Ph_3SnMo(CO)_3cp$	HCl	excess	$PhCl_2SnMo(CO)_3cp$	95	80
$Ph_3SnW(CO)_3cp$	HCl	excess	$PhCl_2SnW(CO)_3cp$	52	80
$Ph_3GeMn(CO)_5$	Br_2		$PhBr_2GeMn(CO)_5$	90	78

a) All reactions carried out at between -15° and room temperature except where noted b) at 110° c) at 60° d) at 80° e) products not separated and the ratio of each was determined by N.M.R. At higher temperatures the ratio reversed there being more of the dichloro species than the monochloro species.

found that the addition of two moles of HCl to one mole of $Ph_3SnFe(CO)_2cp$ gave $PhCl_2SnFe(CO)_2cp$ in over 70% yield,

$$Ph_3SnFe(CO)_2cp + 2HCl \rightarrow PhCl_2SnFe(CO)_2cp + 2PhCl$$

but the analogous reaction of one mole of HCl with one mole of $Ph_3SnFe(CO)_2cp$ gave lower yields (50%) of $Ph_2ClSnFe(CO)_2cp$,

$$Ph_3SnFe(CO)_2cp + HCl \rightarrow Ph_2ClSnFe(CO)_2cp + PhCl$$

The equilibrium for this reaction appears to lie in favour of $PhCl_2SnFe(CO)_2cp$, since the analysis of the crude reaction product $Ph_2ClSnFe(CO)_2cp$ by N.M.R., showed that it invariably, contained some $Ph_3SnFe(CO)_2cp$ and $PhCl_2SnFe(CO)_2cp$, thus necessitating careful recrystalisation in order to obtain a pure product. The lower melting point for this compound (93°) compared to that reported (100-101°) is probably an indication that not all the impurities were removed, although the analyses were acceptable (Table 7-3).

It is interesting to note that in the reactions of the compound $Ph_3SnMn(CO)_5$ with HX or X_2, the species $Ph_2XSnMn(CO)_5$ cannot be obtained (11) since the equilibrium here is also in favour of the species $PhX_2SnMn(CO)_5$ and under more forcing conditions tends to give $X_3SnMn(CO)_5$.

Using this type of reaction the series $Ph_{3-n}Cl_nSnFe(CO)_{2-x}(cp)L_x$ (n = 1 to 3; x = 1 for L = PPh_3, PEt_3, $P(OPh)_3$; and x = 2, for L = $P(OPh)_3$) was also obtained. As before, while the reaction of two moles of HCl with one mole of $Ph_3SnFe(CO)_{2-x}(cp)L_x$ gave only one product in good yield and purity, the 1:1 molar addition of HCl to $Ph_3SnFe(CO)_{2-x}(cp)L_x$ gave an impure product contaminated with both starting material and $Ph_2ClSnFe(CO)_{2-x}(cp)L_x$. The greater sensitivity of these compounds to oxidation in solution resulted in more decomposition upon recrystallisation so that poorer though acceptable analyses were obtained.

By contrast to the reactions of HCl, the cleavage of two phenyltin bonds by the 2:1 molar addition of HBr to $Ph_3SnFe(CO)_2cp$ resulted in a mixture which by analysis of the N.M.R. spectrum was found to contain 75% of $PhBr_2SnFe(CO)_2cp$ and 25% of $Ph_2BrSnFe(CO)_2cp$. There was no indication that any unreacted starting material or $Br_3SnFe(CO)_2cp$ was present. However, the reaction of one mole of HBr with one mole of $Ph_3SnFe(CO)_2cp$ gave an essentially pure sample of $Ph_2BrSnFe(CO)_2cp$. This indicates that the equilibrium for these reactions lies in favour of the monohalo species and not the dihalo species formed in the reaction with HCl. As with the phenylchloro derivatives, these compounds were very sensitive to oxidation and decomposition in solution, thus necessitating careful recrystallisation in order to obtain a pure product.

The reactions of $Ph_{3-n}(C_6F_5)_nSnX$ (n = 1 to 3 and X = $Mn(CO)_5$ or $Fe(CO)_2cp$) with HCl or Cl_2 were also carried out. Excess HCl with $(C_6F_5)_3SnFe(CO)_2cp$ failed to cleave either the metal-metal or metal-carbon bond. The 1:1 or 1:2 molar addition of HCl to $Ph(C_6F_5)_2SnFe(CO)_2cp$ and $Ph_2(C_6F_5)SnFe(CO)_2cp$ respectively after a period of four days gave essentially starting material in 85-90% recovery, and although analysis of the crude reaction mixture by N.M.R. showed that some reaction had occured, the products were not isolated or identified. An excess of HCl on these two compounds invariably resulted in a mixture formed by cleavage of both the phenyl and pentafluorophenyl groups. Chlorine on the other hand, instantly cleaved the metal-metal bond in these and nearly all other metal-iron systems in this work.

Chlorine fails to react with $(C_6F_5)_3SnMn(CO)_5$ and an excess of HCl does not attack either $Ph_2(C_6F_5)SnMn(CO)_5$ or $Ph(C_6F_5)_2SnMn(CO)_5$. However the addition of one mole of chlorine in CCl_4 to one mole of $Ph(C_6F_5)_2SnMn(CO)_5$ gives in 25% yield $Cl(C_6F_5)_2SnMn(CO)_5$, and the similar addition of two moles of chlorine to one mole of $Ph_2(C_6F_5)SnMn(CO)_5$ gives $Cl_2(C_6F_5)SnMn(CO)_5$ in 15% yield.

Since the reactive transition state in these compounds is probably not very different from that involved in the triphenyl derivatives, the selective cleavage of the phenyltin bond in these compounds demonstrates that the Group IV-metal carbon bond in the C_6F_5 compounds is stronger than in the phenyl compounds, and thus in reactions of this type will be retained at the expense of the metal phenyl bond.

These types of cleavage reactions have been rather neglected although they could have considerable promise in the synthesis of other organhalo metal-metal bonded species. The possible formation of mixtures resulting from the simultaneous cleavage of one and two organometal bonds could possibly be prevented by the judicious adjustment of solvents, concentrations and temperatures, but unfortunately the correct combinations cannot be known a priori.

4) Reactions of the Halometal-metal Derivaties with Pentafluorophenyl Lithium

Since about 1962 there has been great interest in the chemistry of the pentafluorophenyl group and this has resulted in the synthesis of a vast number of these compounds (83, 92).

Many of the earlier preparations involved the treatment of the

appropriate metal halide with pentafluorophenylmagnesium bromide (84, 85) in ether, followed by hydrolysis of the reaction mixture by water, dilute mineral acid, or by aqueous NH_4Cl. However this reaction is always accompanied by the formation of heavy black polyfluorophenyl tars which can often only be conveniently removed by column chromatography or by vacuum sublimation.

The ease of preparation of pentafluorophenyl-lithium by the reaction of butyl-lithium with bromopentafluorobenzene (86) or, better still, pentafluorobenzene (87) at -78°, has in recent years made this the reagent of choice. In addition the only by-product from the latter reaction is butane, which is chemically inert, such that the reaction mixture is essentially just a solution of C_6F_5Li in ether. The markedly more reactive nature of C_6F_5Li over that of C_6F_5MgBr, or the recently discovered pentafluorophenylcopper derivatives (88 - 90), makes it more useful than the latter two reagents, although occasionally it will react farther with the products to give other compounds (88).

Despite the great activity in this area, only a few Group IV-transition metal compounds have been prepared. $(C_6F_5)_{3-n}Ph_nSnMn(CO)_5$ (n = 0 to 3) and $(C_6F_5)_2Sn[Mn(CO)_5]_2$ (51) were made by the action of C_6F_5Li on the corresponding chlorides,

$$Cl_{3-n}Ph_nSnMn(CO)_5 + (3-n)C_6F_5Li \xrightarrow[-78°]{\text{ether}} (C_6F_5)_{3-n}Ph_nSnMn(CO)_5 + (3-n)LiCl$$

while the reaction of C_6F_5Li with $Me_2ClSnMn(CO)_5$ gave $Me_2Sn[Mn(CO)_5]_2$ and $Me_2Sn(C_6F_5)_2$ due to spontaneous disproportionation in solution (51). The tris(pentafluorophenyl)silicon derivatives $(C_6F_5)_3SiM'$ (M' = $Mn(CO)_5$, and $Fe(CO)_2cp$) were made by the reaction of $(C_6F_5)_3SiH$ with

the metal carbonyl dimer as described previously (71).

The reaction of $Ph_2ClSnMn(CO)_5$ with C_6F_5Li, gave in addition to the expected product $Ph_2(C_6F_5)SnMn(CO)_5$, an approximately equal amount of $[-Sn(Ph)_2Mn(CO)_5]_2$ which is thought to be formed by the following reaction scheme:

$$Ph_2ClSnMn(CO)_2 + C_6F_5Li \rightarrow Ph_2(Li^+)Sn^-Mn(CO)_5 + C_6F_5Cl$$

$$Ph_2(Li^+)Sn^-Mn(CO)_5 + Ph_2ClSnMn(CO)_5 \rightarrow [-Sn(Ph)_2Mn(CO)_5]_2 + LiCl$$

The reaction of C_6F_5Cl on $Ph_2(Li^+)Sn^-Mn(CO)_5$, as well as the normal substitution of chlorine by C_6F_5 could then give the expected product. However the same reaction using the bromide derivative in place of the chloride derivative gave none of the ditin species, and the only product between the reaction of the analogous chloro-germanium derivative and C_6F_5Li was $Ph_2(C_6F_5)GeMn(CO)_5$.

These observations could be due to the better leaving capacity of bromide relative to chloride since the products of the reaction of Ph_2GeBr_2 or Ph_2GeCl_2 (91) with transition metal carbonyl anions vary quite markedly, but could also be a result of small and subtle differences in the work up of the reaction mixture. The yields for the germanium and tin derivatives were essentially similar but, the yields in the case of the silicon compounds were very much less expecially when one or two phenyl groups were already bonded to the silicon atom. This could be due to the steric crowding of the chorine atoms by the large phenyl group, thus making attack by a pentafluorophenyl group more difficult. However, the construction of molecular models do not show that this is necessarily the case since the $Mn(CO)_5$ species tend to sterically hinder the chlorine atom more than does the phenyl group.

The iron derivatives $Ph_2ClMFe(CO)_2cp$ and $PhCl_2MFe(CO)_2cp$ (M = Si or Ge) failed to undergo metal-halogen exchange by C_6F_5Li even though the tin compounds reacted smoothly to give good yields of $Ph_2(C_6F_5)SnFe(CO)_2cp$ and $Ph(C_6F_5)_2SnFe(CO)_2cp$. The reason for the inert behaviour of the silicon and germanium compounds is not obvious but the explanation does not lie in the increased crowding of the halogen atom by the cyclopentadienyl group, since models show that this group has little or no effect on the stereochemistry of the Group IV atom.

The yields for the reaction of C_6F_5Li with both $Cl_3SiMn(CO)_5$ and $Cl_3SiFe(CO)_2cp$ are both small and least for trichlorosiliconcyclopentadienyldicarbonyliron. An explanation possibly lies in the larger nucleophilicity of the $Fe(CO)_2cp$ group relative to that for $Mn(CO)_5$. This will cause a drift of electrons from the iron to the silicon, thus making attack by C_6F_5Li more difficult. However, the normal reactivity of the tin compounds show that other factors are also important.

It is obvious that while there are very substantial differences in the reaction of metal-metal bonded compounds with C_6F_5Li their origin is not clear, but is obviously a function of the metal-metal bond since the simple halides or organohalides of Group IV show little difference in their reactivity with C_6F_5Li (92, 93), giving in all cases good yields of the halo or organopentafluorophenyl derivatives. The molecular structure and mode of attack of C_6F_5Li in ether is at present unknown, and although the formation in solution of lithio-Group IV-transition metal species could be important, compounds of this type have never been isolated and may not necessarily exist

in all reactions with C_6F_5Li. Any possible ionisation of the metal-chlorine bond or possible attack of C_6F_5Li on the metal carbonyl (94) to give a lithium acyl carbonyl complex must also be taken into account. Until these factors are resolved there is at present no theory to explain the observed differences in reaction of C_6F_5Li with various halogen derivatives of metal-metal bonds.

5. Redistribution Reactions

It is a characteristic property of Group IV metals to undergo exchange of their ligands with those of other Group IV metals. The Group IV metal-metal bonded derivatives are no exception, and sometimes can be usefully used to give products that are not accessible by cleavage reactions, e.g.

$$Ph_3SnMn(CO)_5 + Cl_3SnMn(CO)_5 \rightarrow 2Ph_2ClSnMn(CO)_5 \quad (23)$$

$$Ph_3SnMn(CO)_5 + PhBr_2SnMn(CO)_5 \rightarrow 2Ph_2BrSnMn(CO)_5 \quad (23)$$

This type of reaction was used to prepare $PhCl_2SnFe(CO)_2cp$ from $Ph_2ClSnFe(CO)_2cp$ and $Cl_3SnFe(CO)_2cp$, but the attempted redistribution of $Ph_2ClGeMn(CO)_5$ with $Cl_3GeMn(CO)_5$ gave a mixture of $Ph_2ClGeMn(CO)_5$ and the expected product $PhCl_2GeMn(CO)_5$, which could not be separated. Increasing the temperature or reaction time still gave an impure product. This is one of the drawbacks of this type of reaction since complete reaction cannot be guaranteed and, if a mixture is obtained it is often very difficult to separate the components since the solubilities of both the monohalo and dihalo derivatives are very similar. The melting point of $Ph_2ClSnMn(CO)_5$ made by this method is some five or six degrees below (10) that of the same compound obtained from Ph_2SnCl_2 and $Mn(CO)_5^-$ (52) and suggests that the lower melting

compound was not particularly pure. The impurity $Ph_2BrSnFe(CO)_2cp$, obtained in the reaction of $Ph_3SnFe(CO)_2cp$ with two moles of HBr was removed by a redistribution procedure using exactly the right amount of $Br_3SnFe(CO)_2cp$, calculated from careful integration of the N.M.R. spectra. Extraction and recrystallisation of the product then gave a pure sample of $PhBr_2SnFe(CO)_2cp$.

The tin compounds tend to undergo redistribution more easily than the germanium compounds, whilst the silicon compounds do not redistribute al all. In the attempted preparation of $Ph(C_6F_5)_2SiFe(CO)_2cp$ from $Ph_2(C_6F_5)SiFe(CO)_2cp$ and $(C_6F_5)_3SiFe(CO)_2cp$ extensive charring occured, but fractional crystallisation of the products gave the tris(pentafluorophenyl) derivative as the main constituent of the first crop of crystals and the diphenyl(pentafluorophenyl) derivative as the main constituent of the remaining solution. There was no evidence for the formation of any other product.

In addition many of the compounds that are formed by redistribution reactions, are often more readily prepared in superior yield and purity by use of the appropriate metal carbonyl anion and organo metal halide. Thus, although $PhCl_2GeMn(CO)_5$ could not be obtained in a pure state by redistribution, it was readily available by the reaction of equimolar quantities of $Mn(CO)_5^-$ with $PhGeCl_3$.

The relatively high temperatures needed for these redistribution reactions, often cause quite severe decomposition and may substantially reduce the yield further.

6) Other Preparations

During the last eight years there has been much interest in

the insertion reactions of the lower valent halides of Groups III (95) and IV (96 - 100) into the metal-metal or metal-halogen bonds of a variety of metal carbonyls and their halide derivatives;

e.g. $InBr + Co_2(CO)_8 \xrightarrow{THF} BrIn[Co(CO)_4]_2.THF$ (95)

$GeI_2 + Co_2(CO)_8 \xrightarrow{THF} I_2Ge[Co(CO)_4]_2$ (99)

$GeI_2 + [Fe(CO)_2cp]_2 \longrightarrow I_2Ge[Fe(CO)_2cp]_2$ (101)

$SnCl_2 + ClFe(CO)_2cp \longrightarrow Cl_3SnFe(CO)_2cp$ (98)

$SnCl_2 + ClMo(CO)_2cp \longrightarrow Cl_3SnMo(CO)_2cp$ (98)

$SnCl_2 + [Co(CO)_3L]_2 \longrightarrow Cl_2Sn\ Co(CO)_3L$

(L = CO, PPh_3, $P(OPh)_3$ etc.) (100)

$SnX_2 + [Fe(CO)_2cp]_2 \longrightarrow X_2Sn[Fe(CO)_2cp]_2$

(X = F, Cl or Br) (95)

Tin IV and germanium IV halides (53) also insert into some iron-iron and nickel-nickel bonds, and the reaction of Ph_2SnCl_2 with $Fe(CO)_2cp$ has been shown to give a mixture of $Cl_2Sn[Fe(CO)_2cp]_2$, $PhCl_2SnFe(CO)_2cp$ and ferrocene (102). More recently the stable germanium (II) salts $CsGeCl_3$ (103) and $Me_3NHGeCl_3$ (104) have been used as a source of $GeCl_2$, which has been found to insert into the metal-metal or metal-halide bonds for a number of transition metals (105). The reaction of trichlorogermane with certain transition metal carbonyl halides to give the trichlorogermanium derivative and HCl is thought to arise by the insertion of $GeCl_2$ into the metal halogen bond (73). This is supported by the observation that the dioxane adduct of $GeCl_2$ will insert into the methyl iron bond of $MeFe(CO)_2cp$ to give $MeCl_2GeFe(CO)_2cp$ (106).

Whilst the reaction of Cl_3GeH or $CsGeCl_3$ with $PhFe(CO)_2cp$

gives none of the expected insertion product $PhCl_2GeFe(CO)_2cp$, the reaction of trichlorogermane with $PhFe(CO)_2cp$ gives 50% of $Cl_3GeFe(CO)_2cp$ along with some $ClFe(CO)_2cp$, as recently reported (105).

Thus it appears that in this case Cl_3GeH is acting as a source of Cl_3Ge^+ (or $GeCl_3^-$) which then attacks the phenyliron bond in $PhFe(CO)_2cp$. However, the greater stability of a particular species, or the reactions conditions used, could also influence the course of reaction, since the reaction of $SnCl_2$ with $[Mo(CO)_3cp]_2$ and $MeW(CO)_3cp$ both give the species $Cl_3SnM(CO)_3cp$ (M = Mo or W) (98), and the products formed by the insertion of SnX_2 into the iron-iron bond of $[Fe(CO)_2cp]_2$ have been shown to be very dependent upon the nature of X, the mole mole ration of reactants, and on the reaction conditions (95).

There have been numerous reactions reported that involve the substitution of one or more carbonyl groups by a Group V ligand. Metal-metal bonded derivatives of $Mn(CO)_5$ and $Co(CO)_4$, when heated with a Group V donor ligands undergo ready displacement of one carbonyl group to give the derivatives $Mn(CO)_4L$ (19, 16, 23) and $Co(CO)_3L$, (58, 64, 108) respectively but the substitution of more than one carbonyl group is more difficult and only normally occurs under ultraviolet irradiation (16).

By contrast the metal-metal bonded systems containing the species $Mo(CO)_3cp$ or $Fe(CO)_2cp$ do not undergo carbonyl substitution by phosphines very easily, although compounds of the type $IFe(CO)_2cp$, $IMo(CO)_3cp$, and $[Fe(CO)_2cp]_2$ will react with certain phosphines (L) in refluxing benzene to give the monosubstituted complexes $IFe(CO)(cp)L$ (110) $IMo(CO)_2(cp)L$ (109) and $Fe_2(CO)_3(cp)_2L$ (110) respectively.

Compounds of the type $XFe(CO)_2cp$ (X = halide) give when X = Cl or I, the ionic compounds $Fe(CO)_2(cp)L^+X^-$ as well as the normal substitution product (11). The U.V. irradiation of $MeFe(CO)_2cp$ with various Group V ligands can, depending upon the conditions, give either MeFe(CO)(cp)L or MeCoFe(CO)(cp)L (112); the latter compound resulting from the insertion of CO into the methyliron bond.

Another type of reaction that seems to be almost exclusive for some silicon-cobalt (58, 108, 113) or silicon-manganese (58, 59) bonded derivatives is the cleavage of the metal-metal bond by the ligand to give a cationic Group IV species,

$$R_3SiM' + L \rightarrow R_3SiL^+M^-$$

(R = H or Me; $M' = Mn(CO)_5$ or $Co(CO)_4$ and L = PMe_3 or NMe_3 etc.)

although the same reaction carried out under the influence of U.V. irradiation gives the normal monosubstitution product.

Substituted compounds of the type $R_3MFe(cp)L_2$ R = Ph, Me, M = Si or Sn, L = Co, PPh_3, $P(OPh)_3$, etc. can however only be made by the ultraviolet irradiation of the corresponding dicarbonyl with the Group V ligand, since the thermal reaction of these two species does not occur. Chelating phosphines sometimes replace both carbonyl groups (115) but stereochemical factors can prevent this regardless of the length of reaction time, and only the monocarbonyl species results even though the exactly analogous reaction with a monodentale ligand gives the expected disubstituted compound (114). It is also clear that the yields and products of these reactions are notoriously dependent (13, 14, 30) upon the conditions and output power of the irradiating lamp and can often be greatly improved by use of a higher powered lamp for a shorter time.

CHAPTER 3

MOSSBAUER SPECTROSCOPY

1) Introduction

Although the Mossbauer effect was discovered for the 191 isotope of iridium in 1957, it was not until 1960 when it was shown that iron (57) also exhibited this effect, that it began to be used to study chemical problems. Shortly afterwards the 119 isotope of tin was also shown to exhibit this phenomenon, and although several other elements show a Mossbauer effect, by far the greatest percentage of work has been carried out on tin and iron compounds.

The Mossbauer effect is the resonant absorption of gamma-rays, which are emitted as the nucleus drops from an excited state to one of lower energy. When these rays fall upon the same nucleus in a different compound some of them may be absorbed and the second nucleus excited. In practice, only a small fraction of the exciting radiation will be absorbed because the exact matching of the excitation energy of the nucleus and the energy of the incident γ-photon is required. Any mismatching of the nuclear excitation energy and the energy of the incident beam will destroy the resonance. This is mainly caused by the recoil of the absorbing or emitting nuclei which will cause a difference in the energy of the γ-photon from the nuclear excitation energy by an amount equal to the recoil energy.

In order to observe a significant absorption there must be a fraction of nuclei that will emit or absorb without recoil, for if the recoil energy is equal to or larger than the natural line widths no resonance will be observed. Therefore the nucleus is placed in a closely packed lattice in which the lowest vibrational excitation energy is greater than the recoil energy. The absorption can be further improved by cooling the absorbing nuclei to 80°K, which also serves to increase the recoil free fraction.

Any interaction of the nucleus with the surrounding electrons is sufficient to destroy the resonance, but this can be restored by applying a variable velocity to the source, in which the energy of the γ-rays seen by the sample are varied according to the Doppler effect. Because of the extremely small line width of the incident γ-ray only a few millimeters per second are needed to restore resonance.

In practice a Mossbauer isotope with a significant recoil-free fraction must have a low energy excited state, preferably accessible by the spontaneous decay of the parent isotope of reasonably long half-life, and of small enough line width, to give reasonable resolution.

Usually however, Mossbauer sources do not emit a single γ-ray, but the unwanted γ-rays and other X-rays can be conveniently removed by electronic devices or filters. The nuclear physics of tin and iron compounds are such that the percentage of Mossbauer atoms do not need to be enriched above their natural level, i.e. 2.2% for ^{57}Fe , and 8.6% for ^{119}Sn respectively. This, and the large variety of compounds in many different structural types is perhaps the reason that so much emphasis has been placed on these two isotopes.

Any interaction of the nucleus with its surrounding environment will give rise to shifts and splittings of the absorption, the origin of which will be examined individually.

2) The Isomer or Centre Shift

The centre shift (C.S.) is the extent to which the maximum absorption is shifted from zero velocity, due to interaction with the nucleus with its immediate electronic environment. This interaction results in a small change of energy between the ground and excited states in the compound relative to that in the free atom, and a Doppler velocity will have to be supplied to the source to observe the resonance.

The centre shift (δ) is found from perturbation theory, to depend on the overlap of nuclear density with s electron density such that,

$$\delta = K\frac{\delta R}{R}\left[\,|\psi(0)_s|^2_a \;-\; |\psi(0)_s|^2_s\,\right]$$

where K is a constant, R the radius of the nucleus δR the difference between the excited and ground state-radii and $|\psi(0)_s|_a$ and $|\psi(0)_s|_s$ are the total s electron densities at the absorber and source respectively. The electrons which most closely penetrate the nucleus are the s electrons, and although p and d electrons can effect the s electron density at the nucleus by shielding, their effect is relatively small such that the centre shift is dependent mainly on the s electron density at the nucleus.

The sign of $\delta R/R$ is very important. For some isotopes, e.g. ^{57}Fe, $\delta R/R$ is negative, and if $|\psi(0)_s|^2_a < |\psi(0)_s|^2_s$, a positive centre shift is observed and indicates a net <u>decrease</u> in s electron density

at the absorber. For other isotopes, e.g. ^{119}Sn, $\delta R/R$ is positive, and if $|\psi(0)_s|^2_a > |\psi(0)_s|^2_s$, a positive centre shift results and indicates an increase in s density at the absorber.

Although p and d electrons do not effectively penetrate the nucleus, changes in both the p and d electron density can affect the centre shift by indirect means. For free iron nuclei an increase in 3p and 3d electron density causes a marked decrease in the 3s density and increases the centre shift. For free tin nuclei an increase in 5p electron density will cause a decrease in the effective s electron density and decrease the centre shift.

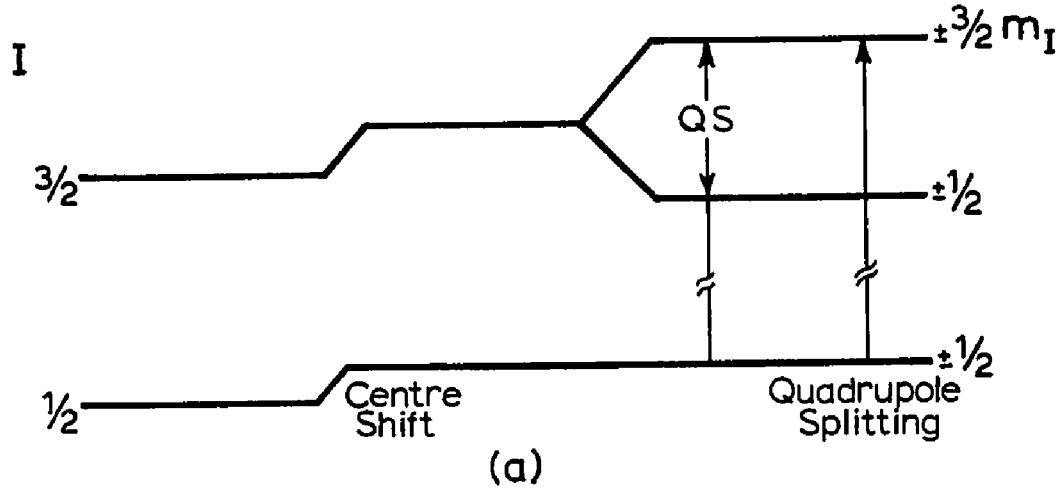
In a molecule however, the situation becomes even more complex because of the changes in valency and in s, p and d populations due to covalent bonding. Although these effects can be calculated, the calculations are neither very accurate, nor very rigorous so relative centre shifts are usually considered.

3) The Quadrupole Splitting

If the nucleus has a spin (I) of more than ½ and is non-spherical, then the interaction of a non-cubic extranuclear electric field with the nuclear charge density results in the splitting of the nuclear energy levels. For tin and iron I = 3/2 such that the ±3/2 level is split by an amount equal to the quadrupole splitting and results in a two line spectrum from the two allowed transitions. This is shown in Figure 3-1. The centre shift relative to the source, is then the centroid of these two peaks from the point of zero velocity. For iron and tin nucleii the quadrupole splitting (Q.S.) is given by:

$$Q.S. = \tfrac{1}{2}e^2qQ\left(1 + \frac{\eta}{3}\right)^{2\frac{1}{2}}$$

Nuclear Energy Levels and the Quadrupole Splitting a) absorber energy levels: exicted level I = 3/2 split into two by quadrupole interaction and b) the resultant spectrum



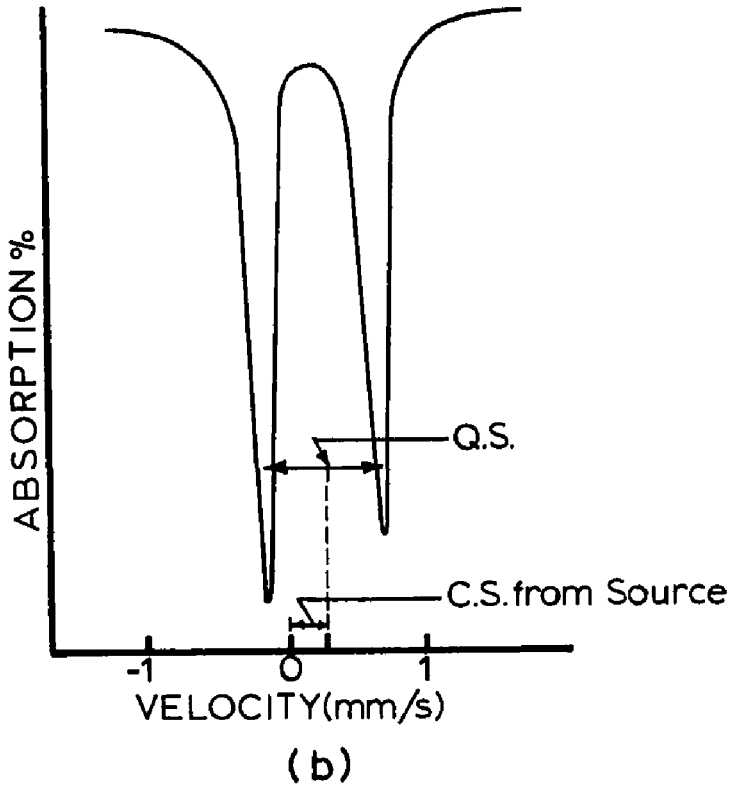


Figure 3-1

where eQ is the nuclear quadrupole moment; eq the electric field gradient along the axis of quantisation, and η the assymmetry parameter.

The magnitude of the quadrupole splitting is thus proportional to the electric field gradient (E.F.G.) tensor which interacts with the quadrupole moment of the nucleus and measures the distortion from cubic symmetry of the electron distribution about the Mossbauer nucleus. In theory, the E.F.G. can be assumed to be derived from point charges and can be defined by three components of electric potential V_{xx}, V_{yy}, and V_{zz} such that η, the assymmetry parameter is equal to $\frac{V_{xx}-V_{yy}}{V_{zz}}$ and $V_{zz}>V_{yy}>V_{xx}$. Thus η is constrained to have values of between 0 and 1. In practice it is convenient to choose V_{zz} to lie along the axis of highest symmetry in the molecule such that $\eta = 0$, but for some molecules this is impractical, and η is greater than 0, but still less than 1.

It is of course impossible to measure η and q directly from a simple two line spectrum, since there is only one equation relating the two unknowns. Also Q can either be positive or negative and thus the Q.S. and q need not have the same sign. However, the sign of the quadrupole splitting and η can be measured by orientating all the molecules in a sample in the same direction i.e. using a single large crystal and observing the variation in the intensity of each absorption with the variation of the sample with respect to the incident beam. It is however more convenient to place the powdered sample, at very low temperatures, in a large external magnetic field which completely removes all the degeneracy in the nuclear energy levels. Since the

E.F.G. axes are randomly orientated with respect to the magnetic field, superimposed spectra result. For iron, and if $\eta = 0$ or small, a doublet-triplet spectrum results and if the doublet is at higher positive velocities then Q.S. and q are positive. As η approaches unity the spectrum changes into a triplet-triplet spectrum and using detailed computing methods an estimate of η, q and the Q.S. can be made. For tin, however, a doublet-quartet spectrum is observed in an applied field, and if the doublet is at higher positive velocities Q.S. is positive but q is negative, since Q for ^{119}Sn is also negative.

It is convenient to divide q into two parts, q lattice, which is the contribution for the external ligand charges and q valence which is the contribution from the valence electrons such that

$$q = (1 - \gamma_\infty)q_{lattice} - (1 - R)\,q_{valence}$$

where γ and R are the Stemhiemer antishielding factors, which although they do affect the magnitude of q do not affect its sign.

However, since valence orbital populations are difficult to calculate, q_{val} for p electrons is written as,

$$q_{val} = Kp\left[-N_{pz} + \tfrac{1}{2}(N_{px} + N_{py})\right]$$

where Kp is a constant and Np the orbital population.. Similarly for d electrons,

$$q_{val} = Kd\left[-N_{dz^2} - N_{dx^2-y^2} + N_{dxy} - \tfrac{1}{2}(N_{dxy} + N_{dyz})\right]$$

where Kd is another constant.

Thus when all three p orbitals or the component orbitals of the t_{2g} and/or eg levels have equal populations then $q_{val} = 0$. Similarly q_{val} equals zero in a octahedral or tetrahedral array of six charges

of equal magnitude. Compressing the axial ligands in an octahedral structure gives a negative value for q_{lat}, whilst compression of the equatorial ligands gives a positive value for q_{lat}, but a concentration of charge along the z axis of the E.F.G. gives a negative q.

To systematise Q.S. data, the point-charge model (34) was developed in which each ligand is assigned a charge, the magnitude of which represents the contribution of that ligand to the electric field gradient (E.F.G.). Since the E.F.G. is expressed as $q_{val} + q_{lat}$, a separate charge is given to each such that the sum of the two equals the partial field gradient (L). Thus, for a polyatomic molecule, the E.F.G. tensor can be written in terms of polar coordinates to include all nine axial components summed over all ligands. For a given structural type η and V_{zz} and, hence Q.S. can thus be calculated since,

$$Q.S. = \tfrac{1}{2}eV_{zz}Q(1 + \eta^2/3)^{\frac{1}{2}}$$

Examples of this type of calculation have been reported for all the commonly encountered geometries about Sn(IV) (34, 116, 120) and low spin Fe(II) nuclei (34). In such a treatment it is assumed that the value of L is constant for all compounds in a given valency state, and although this is not strictly true it gives a good semi-quantitative guide to the relative values of quadrupole splittings.

Clark (116) and Bancroft (112) have used molecular orbital approaches to calculate quadrupole splittings, in which, instead of considering each ligand as a point charge, the effect of the ligand upon the populations of the iron (or tin) atomic orbitals is taken into account. This treatment is more rigorous than the simple

additivity model, but the sign and relative magnitude of the ligand partial field gradients are the same as those derived from real compounds using the point-charge model. The molecular orbital approach has also been used to allow for the known distortions from idealised symmetry as determined by x-ray crystallographic studies (116). However, the values of the Q.S. thus obtained may or may not agree with observed value and do not necessarily give a more accurate value for the partial field gradient over that found from idealised symmetry.

4) Organotin Derivatives - Quadrupole Splitting

Until quite recently two major factors have hindered any systematic interpretation of Sn(IV) quadrupole splittings. Firstly, the origin of the E.F.G. could be ascribed to either σ or π bonding assymmetrics or $q_{lattice}$ effects, and secondly, the change of magnitude of the quadrupole splitting with a change in coordination number could not predicted. After a great deal of argument in the literature it was suggested (119) that, in general, the quadrupole splittings of tin (IV) compounds arise from a σ orbital imbalance due to inequalities in bond polarities and that π bonding effects can be neglected. This is because $q_{valence}$ is proportional to one over the cube of the radius of any orbital such that any d orbital which might π bond with any other atom will have about one hundred times less significance than the p orbital in the same shell, and will thus have a minimal effect on the quadrupole splitting. It is also evident that in order to compare changes in bond character isostructural series must be studied for any change in the coordination number will drastically affect the quadrupole splitting.

On the basis of the point charge formalism, and the additivity model, it is possible to assign a partial quadrupole splitting (p.q.s.) parameter of a ligand L such that

$$(p.q.s.)_L = \tfrac{1}{2}e^2|Q|\ L$$

where $|Q|$ is the magnitude of the nuclear quadrupole moment and L the partial field gradient. For a standard, the p.q.s. of chlorine in $SnCl_5^-$ (120) was initially taken as a reference point from which the p.q.s. values of other ligands could be calculated for compounds of known structure.

However, from the molecular orbital theory of quadrupole splittings (117) it is more proper and realistic to derive p.q.s. values of ligands within a particular geometry around the tin. In nearly all cases the value predicted by this approach agrees with that observed experimentally, but when agreement is not observed the reason can be usually found in either changes in coordination number, or a large deviation from regular geometry.

For compounds that have more than one geometric isomer, the predicted value of the quadrupole splitting varies according to the structure (118, 121). The Q.S. value that most closely agrees with the observed value is often, but not always, the one that is born out by other studies.

5) Results and Discussion

The tin Mossbauer parameters have been published for a number of tin-transition metal systems of the type R_3SnM' (R = Me, Ph, Cl etc., and M' = transition metal moeity) (114, 122-133), but there has been little attempt at explaining the quadrupole splittings.

Crystallographic studies (134 - 138) show that for all the compounds studied in this thesis the tin atom is four coordinate with no abnormally short non-bonded inter or intramolecular distances.

The observed quadrupole splittings listed in Table 3-1 for compounds of the type $R_{3-n}Y_nSnM'$ (R = Ph, Y = Cl, Br, or C_6F_5, n = 0 to 3 and M' = $Mn(CO)_5$ or $Fe(CO)_2cp$) show that the order of increasing Q.S. invariably is,

$$RX_2SnM' > R_2XSnM' > X_3SnM' > R_3SnM'$$

This order can be readily rationalised by application of the partial quadrupole splitting treatment (115) for tetrahedral tin compounds, in which replacement of one of the ligands R by another ligand X which has very different bonding properties will cause a large increase in the quadrupole splitting. This marked change in the different bonding properties of the ligands is also verified by the increase in distortion around the tin atom in going from the least distorted R_3SnM' (134-135) systems where the RSnR and RSnM' angles are close to that for tetrahedral symmetry to the distorted X_3SnM' (136, 138) and even more distorted RY_2SnM' systems (137).

Clark et al derived the p.q.s. values for chlorine, bromine and phenyl to be 0.00, 0.00 and -1.26 mm/s respectively based upon careful analyses of some other Q.S. values obtained from the literature. The value for chlorine or bromine was arbitarily placed at zero since there was some uncertainty to its true value. This will, however, not affect the predicted value of the Q.S. since this is dependent upon the relative p.q.s. values and not on its absolute magnitude.

Errors in the p.q.s. values arise as a result of using distorted

compounds to derive values for the p.q.s. of other ligands. However, although these distortions can be taken into consideration (115, 117, 129, 131, 132) they are best ignored and a deviation of 0.4 mm/s between the observed and predicted values of the Q.S. for a given compound is considered acceptable.

In this work the p.q.s. values for $Mn(CO)_5$ and $Fe(CO)_2cp$ were derived from the least distorted triphenyltin derivatives and are thus substantially different from those derived by Clark. These values, listed in Table 3-2, are generally more internally consistant and give better predictions of the Q.S. The value for the p.q.s. of C_6F_5 calculated (139) from the analysis of the Q.S. for the series $R_{3-n}Sn(C_6F_5)_n$ (R = Me or Ph, and n = 0 to 2) (117) and again is found to be higher to the previous value of 0.7 mm/s.

In order to place the p.q.s. parameters on the same scale it is necessary to use as a reference point a compound of known sign. The origin of the Q.S. of $Cl_3SnFe(CO)_2cp$ has been shown to be positive (131) and of the p.q.s. if chlorine is placed at zero then the p.q.s. of $Fe(CO)_2cp$ must be negative. Conversely the sign of Q.S. if $Bu_3SnFe(CO)_2cp$ has been shown to be negative (131) and since the Q.S. is very small, the p.q.s. of butyl is also negative but greater than that for $Fe(CO)_2cp$. Therefore it is assumed that the signs of the Q.S. for the triphenyltin and trichlorotin species in this work are also negative and positive respectively, and using these as reference points the signs of the Q.S. and the magnitude of the p.q.s. values have been determined.

The agreement between the predicted and observed values of the

quadrupole splitting listed in Table 3-3 for most compounds is good to within 0.25 mm/s and well within the 0.4 mm/s variation considered acceptable (117).

For the compound $PhCl_2SnFe(CO)_2cp$ the known distortion can be taken into account. Recalculation then gives the Q.S. as 2.79 mm/s (115), in excellent but perhaps fortuitous agreement with the observed value of 2.84 mm/s, although by Clark's molecular orbital method (117) a smaller quadrupole splitting results.

However, the lack of agreement between the observed and predicted values for $(C_6F_5)_3SnMn(CO)_5$, $(C_6F_5)_3SnFe(CO)_2cp$, $Br_3SnFe(CO)_2cp$ and $Br_3SnMn(CO)_5$ suggests that it can be sometimes misleading to infer degrees of association or changes in the bonding properties of the ligands from small changes in the quadrupole splitting (140). There is no obvious reason for these discrepancies, but consideration of the possible distortions using the point charge or molecular orbital treatment does not improve the values (139).

The rationalisation of the p.q.s. values has been made in terms of the p donor ability of the ligand (118), which increases as the p.q.s. value becomes more negative. The s shell is spherically symmetric and so cannot have an affect on the Q.S. Clark has shown that due to the large increase in the radial size of the d orbital relative to the p orbital, the contribution to the Q.S. from the former is very small and can be neglected (117).

Thus the p.q.s. value of a ligand is solely dependent upon the population of the $\sigma 5_{pz}$ bonding orbital directed along the metal-metal bond. The p donor ability of a ligand is defined as the electron

population of the tin-ligand orbital as is composed of a) the p character of the tin ligand bond, and b) the donor ability of the ligand. For the ligands in this work the p donor ability increases in the order,

$$Cl, Br < C_6F_5 < Mn(CO)_5 < Fe(CO)cp < Ph$$

This series may, or may not, agree with σ donor strengths derived from other physical measurements since it is only sensitive to σ_p electron density and is virtually independent of any s, d or π character in the tin-ligand bond. Some recent work on some tin-cobalt compounds show that the p.q.s. for $Co(CO)_4$ is very low (141) and, for the transition metal carbonyls in general, the p.q.s. values increase in the same order as their nucleophilicities, i.e.

$$Co(CO)_4 < Mn(CO)_5 < Fe(CO)_2cp \quad (50, 72)$$

6. Organotin Derivatives - Centre Shifts

For tin(IV) halides and their complexes, the centre shift decreases as the average electronegativity of the ligand increases, but at the same time will decrease on increasing the coordination number (34).

However, the centre shifts of organotin compounds do not show any dependence on bond polarity, although some correlation between the C.S. values and Mulliken electronegativities for the species Me_3SnX and $Me_2SnX_4^{2-}$ (X = Cl, Br and I) (144) have been found.

However, any change in the number of organic groups around the tin in compounds of the type $RnSnX_{4-n}$ (R = alkyl or aryl, X = halide and n = 0 to 3) do not greatly affect the C.S. and are virtually independent of the nature of R and X (34).

Two explanations have been proposed for this insensitivity, the

first of which is that the substitution of an electronegative ligand causes a rehybridisation of the bonding tin orbitals which results in an asymmetric distribution of the 5p electrons and a net reduction in the s character of the Sn-X bond, but no loss of charge (145). This is however, at variance with the N.Q.R. spectra of these compounds (147) which can be best explained by assuming that a loss of charge does occur. Alternatively, it was proposed that the substitution of a more electronegative substituent removes charge from the valence shell, thereby increasing the positive charge on the tin (145). This in turn causes a deshielding and contraction of the 5s orbital and increases the C.S. more than would be expected from consideration of the first effect alone.

In summary, it may be said that the factors that control the C.S. values for organotin compounds are poorly understood, and substantially new theories are needed to rationalise the observed trends.

7) Results and Discussion

For the tin-transition metal bonded compounds given in Table 3-1 the centre shift increases as the relative electronegativity of the ligands bonding to tin increases. Previous results for the systems $XnSnM'_{4-n}$ (X = Ph, Cl or Br and M' = $Mn(CO)_5$ or $Fe(CO)_2cp$) indicate that increasing C.S. values reflect increasing s character of the tin ligand bond in the order Cl<Br<R<M (122, 124, 128, 129). The ^{55}Mn (128) and ^{1}H N.M.R. data (122) support this interpretation and the generally larger C.S. values for the tin-iron compounds compared with the tin-manganese compounds indicate that the Sn-Fe bond has a larger s character than the Sn-Mn bond.

However, from the analysis of the quadrupole splitting data, the $Fe(CO)_2cp$ group is a better p donor than $Mn(CO)_5$ and hence would tend to decrease the C.S. values of a tin-iron compound with respect to the analogous tin-manganese compound. A similar argument also applies to the tin-methyl and tin-phenyl bonds, the C.S. values for the Sn-Me compounds are larger than those for the Sn-Ph compounds (147), indicating a greater s character in the Sn-Me bond over the Sn-Ph bond. The p-donor strengths indicate that methyl is a better p donor than phenyl and so would be expected to have less s character in its bond to tin.

The variation in C.S. values for pentafluorophenyltin bonds indicates that the phenyltin bond has a higher s character than the C_6F_5Sn bond (149), but since the p donor series indicates that C_6F_5 is a worse p donor than Ph, the pentafluorophenyltin compounds should have a larger centre shift than the analogous phenyltin compounds.

These trends can however be rationalised by considering just the effect of p electron density. Firstly, the replacement of a ligand by one of poorer p donor capacity will increase the s electron density by deshielding and increase the C.S. Secondly, in opposition to this, if there is appreciable s character in the tin ligand bonds, replacement of a ligand by one of lower s character will decrease the centre shift, since any concomitant increase in p character will have a negligible effect on the centre shift. Thus, the centre shift will increase or decrease according to the relative s character in the tin ligand bond. Thirdly, in tin-transition metal systems the replacement of a ligand by one of greater p

character will cause an increase in the s character of the tin-metal bond, increase the square of the s density at the tin nucleus and, hence increase the C.S. much more markedly than would be expected from the first effect. Thus, in the series $(C_6F_5)_nSnPh_{4-n}$, the centre shift decreases from 1.22 mm/s observed for Ph_4Sn to 1.04 mm/s observed for $(C_6F_5)_4Sn$ (149). This is due mainly to the first effect, since the greater electron withdrawing power of C_6F_5 relative to Ph will decrease the 5s electron density on the tin. However, the centre shift for the series $Ph_{4-n}Cl_nSn$ (n = 0 to 2) increases from Ph_4Sn (148, 149) to Ph_2SnCl_2 (145) (1.38 mm/s) because of the first effect, in which the electron withdrawing chlorine withdraws mostly 5p electron density from the tin-chlorine bond, which in term increases the s density at the tin nucleus, and increases the centre shift.

For tin-metal bonds the centre shift increases more markedly when replacing Ph by Cl or Br than it does when replacing Ph by C_6F_5, but in all cases the increase in C.S. is more marked than for compounds containing no Sn-metal bonds. This is due to the large degree of s character in the tin-metal bond (122) which effectively enhances any increase in the centre shift due to withdrawal of p electron density by replacement of Ph by Cl, and completely obscures any decrease of C.S. due to substitution of Ph by C_6F_5.

From the ordering of the increase in C.S. values, a series of ligand-tin s character may be derived. The s character of a ligand is defined as the percentage s character in a tin-ligand bond and is not the same as s donor strength which just relates the amount of s density a ligand is putting into a bond. For the ligands

described in this work the order is $Cl,Br<C_6F_5<Ph<Mn(CO)_5<Fe(CO)_2cp$. Thus the Sn-Fe bond has the greater amount of s character and the Sn-Cl bond has the least, and can be effectively considered to be largely p in character. It will be noticed that the ordering of p donor ability and the s character of the tin-ligand bonds are not the same, but there is no reason why they should be since it is difficult to see why the two should be related to each other.

The greater amount of s density in the tin-iron bond will, because of the smaller radial size of the s orbitals, serve to decrease the Sn-Fe bond length. A progressive shortening of the Sn-Fe bond length has been observed in the series $Ph_{3-n}Cl_nSnFe(CO)_2cp$ (n = 0 to 3), from that in $Ph_3SnFe(CO)_2cp$ (2.54Å), (135) to that in $Ph_2ClSnFe(CO)_2cp$ (2.50Å), (137) and finally to that in $PhCl_2SnFe(CO)_2cp$ (137) and $Cl_3SnFe(CO)_2cp$ (136), where the Sn-Fe bond length has the same value of 2.47Å. This appears to be a limiting value in spite of the fact that the s character of the metal-metal bond in $Cl_3SnFe(CO)_2cp$ is greater than in $PhCl_2SnFe(CO)_2cp$, but this difference is less than that for the other members of the series. This may explain in part, why a plot of the C.S. against the number of halogen atoms changes regularly up to $PhCl_2SnFe(CO)_2cp$ but falls off dramatically from $PhCl_2SnFe(CO)_2cp$ to $Cl_3SnFe(CO)_2cp$. The similarity of the C.S. values for $Cl_3SnFe(CO)_2cp$ and $Br_3SnFe(CO)_2cp$ can also be explained by observing that the Sn-Fe bond length in both compounds is the same at 2.47A (137, 138).

It is reasonable to suppose that if the Sn-Fe bond length is decreasing with increasing s character in this bond, the Sn-Cl bond

is increasing in p character . and on this basis should show an increase in bond length. However, this is not observed but it is noticed that the Sn-Cl bond length of 2.36 to 2.39A observed in these compounds is longer than that in Ph_2SnCl_2 (2.35Å) (150) or in Ph_3SnCl (2.32Å) (151). This constant value for the Sn-Cl bond length for the tin-iron series possibly can be explained by assuming that the expected increase in p character may have already been reached upon the introduction of the first chlorine group.

The influence of the p donor strength upon the s character of the tin-ligand bond is also applicable in other tin-transition metal systems. Thus, for the system $X_3SnFe(CO)_2cp$ (X = halide, NCS, $MeCO_2$, or HCO_2) (129) it can be shown that NCS is a much poorer p donor than HCO_2 such that the substitution of NCS for HCO_2 causes an increase in s density at the tin nucleus and increases the C.S. for $(NCS)_3SnFe(CO)_2cp$ relative to that for $(HCO_2)_3SnFe(CO)_2cp$. In addition the very much smaller range, but higher values for the C.S. in the series $X_2Sn[Fe(CO)_2cp]_2$ indicates that the large s character of the Sn-Fe bond controls the C.S. value more than does the Sn-X bond. This is further exemplified by the series $Ph_nSn[Fe(CO)_2cp]_{4-n}$ (n = 1 to 3) (127) in which the C.S. increases as n decreases due to an increase in s density on the tin nucleus from each additional iron atom. The series $Me_3SnM(CO)_3cp$ (M = Cr, Mo, or W) (130) show that from the analysis of the Q.S. values, $W(CO)_3cp$ is a better p donor than is $Cr(CO)_3cp$, such that the p electron density of the Sn-W bond is more than that in the Sn-Cr bond. The C.S. for $Me_3SnW(CO)_3cp$ should then be less than that for $Me_3SnCr(CO)_3cp$ and

this is observed experimentally.

These examples show the generality of such approaches in discussing the electron density around the tin, although the comparison of two ligands that have similar p.q.s. values should be avoided since the error in this value may obscure or reverse the trend found from simple examination of the results.

Considering the structural data, one would expect that the greater the differences in s character in the tin-ligand bond, the greater the deviation from tetrahedral symmetry, and the smaller the L-Sn-L bond angle for the bond of lowest s character. This idea was originally proposed by Zuckerman et al (122) and is elegantly exemplified by more recent crystal structures. The RSnX and XSnM' bond angles for some of these systems are given in Table 3-4. Thus $Ph_3SnMn(CO)_5$ is only slightly distorted from tetrahedral symmetry (134) since Ph and $Mn(CO)_5$ have similar s characters, but is in contrast to $Cl_3SnFe(CO)_2cp$ (136) which is very distorted, and due to the widely differing s character of the chlorine and $Fe(CO)_2cp$ groups. Thus the distortions will be expected to increase in the order $Ph_3SnMn(CO)_5<Ph_3SnCl<Ph_3SnFe(CO)_2cp<Cl_3SnFe(CO)_2cp<PhCl_2SnFe(CO)_2cp$ and are qualitatively born out by the crystal structures. The compounds $X_2 Sn M_2$ (X = Me, Cl; M = $Fe(CO)_2cp$ and $Mn(CO)_5$) also show increasing distortion as the differences in s character become larger. Thus $Ph_2Sn[Mn(CO)_5]_2$ (152) is the least distorted and $Cl_2Sn[Fe(CO)_2cp]_2$ (153) is the most distorted, and that the distortions in Ph_2SnCl_2 (150) are similar to those in $Me_2Sn\ Fe(CO)_2cp$ (154) since the differences in s character between the two ligands for each molecule can be considered to be equal, although any quantitative measurement of their respective

Table 3-1

^{119}Sn Mossbauer Data at 80°K

	Compound	c.s. mm/s[a]	Q.S. mm/s[a]	Γ_1[b]	Γ_2[b]
1)	$Ph_3SnMn(CO)_5$	1.35 (1.41)[c]	0.41±0.10(0)	0.97	1.04
2)	$Ph_2(C_6F_5)SnMn(CO)_5$	1.45	0.95	1.11	1.02
3)	$Ph(C_6F_5)_2SnMn(CO)_5$	1.45	1.06	1.15	1.01
4)	$(C_6F_5)_3SnMn(CO)_5$	1.44	0.99	1.04	1.08
5)	$Ph_3SnFe(CO)_2cp$	1.39	0.32±0.10 [0.0][d]	1.06	1.06
6)	$Ph_2(C_6F_5)SnFe(CO)_2cp$	1.48	0.93	1.21	1.03
7)	$Ph(C_6F_5)_2SnFe(CO)_2cp$	1.48	1.37	1.14	0.99
8)	$(C_6F_5)_3SnFe(CO)_2cp$	1.39	1.21	0.86	1.11
9)	$Ph_2BrSnFe(CO)_2cp$	1.61	2.52	1.27	1.17
10)	$PhBr_2SnFe(CO)_2cp$	1.73	2.65	0.98	1.04
11)	$Br_3SnFe(CO)_2cp$	1.86	1.63	1.14	0.92
12)	$Ph_2ClSnMn(CO)_5$	1.61 (1.57)	2.50 (2.36)	1.13	1.11
13)	$PhCl_2SnMn(CO)_5$	1.63 (1.68)	2.52 (2.62)	1.26	1.23
14)	$Cl_3SnMn(CO)_5$	1.65 (1.68)	1.60 (1.57)	1.18	1.13
15)	$Ph_2BrSnMn(CO)_5$	1.58 (1.59)	2.31 (2.28)	1.12	1.06
16)	$PhBr_2SnMn(CO)_5$	1.75 (1.80)	2.65 (2.63)	1.09	1.00
17)	$Br_3SnMn(CO)_5$	1.76 (1.79)	1.53 (1.41)	1.23	0.98
18)	$Ph_2ClSnFe(CO)_2cp$	1.57	2.40 [2.34]	1.31	1.16
19)	$PhCl_2SnFe(CO)_2cp$	1.70	2.84 [2.56]	1.15	1.12
20)	$Cl_3SnFe(CO)_2cp$	1.73	1.83 [1.80]	1.18	1.12

a) Relative to $BaSnO_3$; the errors are ±0.02 mm/s except where noted
b) Line width at half height; errors are ±0.05 mm/s
c) Numbers in parentheses are from reference 128
d) Numbers in square brackets are from reference 133

Table 3-2

Partial Quadrupole Splitting Values

Ligand	p.q.s (mm/s)	Reference
Cl, Br	0.00	117
Ph	-1.26	117
C_6F_5	-0.76	142
$Mn(CO)_5$	-0.97	142
$Fe(CO)_2cp$	-1.08	142
$Co(CO)_4$	-0.71	141

From reference 117 the p.q.s. values are C_6F_5= -0.70, $Mn(CO)_5$ = -0.79, and $Fe(CO)_2cp$ = -0.91 (mm/s).

Table 3-3

Predicted and Observed Values of the Quadrupole Splitting

a) For compounds in this work:

Compound	Q.S. calc (mm/s)	|Q.S.| obs (mm/s)	Reference
$Ph_3SnMn(CO)_5$	-0.50	0	133
$Ph_3SnMn(CO)_5$	-0.58	0.41	142
$Ph_2(C_6F_5)SnMn(CO)_5$	-0.97	0.95	142
$Ph(C_6F_5)_2SnMn(CO)_5$	+0.95	1.06	142
$(C_6F_5)_3SnMn(CO)_5$	+0.42	+0.99	142
$Ph_3SnFe(CO)_2cp$	-0.26	0	133
$Ph_3SnFe(CO)_2cp$	-0.36	0.32	142
$Ph_2(C_6F_5)SnFe(CO)_2cp$	-0.94	0.93	142
$Ph(C_6F_5)_2SnFe(CO)_2cp$	+0.99	1.37	142
$(C_6F_5)_3SnFe(CO)_2cp$	+0.64	1.21	142
$Ph_2ClSnFe(CO)_2cp$	-1.99	2.34	133
$Ph_2ClSnFe(CO)_2cp$	-2.42	2.54	142
$PhCl_2SnFe(CO)_2cp$	+2.24	2.56	133
$PhCl_2SnFe(CO)_2cp$	+2.72	2.84	142
$Cl_3SnFe(CO)_2cp$	+2.16	1.83	142
$Cl_3SnFe(CO)_2cp$		1.80	133
$Ph_2ClSnMn(CO)_5$	-2.39	2.50	142
$PhCl_2SnMn(CO)_5$	+2.62	2.52	142
$Cl_3SnMn(CO)_5$		1.56	133
$Cl_3SnMn(CO)_5$	+1.94	+1.60	142
$Ph_2BrSnMn(CO)_5$	-2.39	2.31	142
$PhBr_2SnMn(CO)_5$	+2.62	2.65	142
$Br_3SnMn(CO)_5$	+1.94	1.53	142
$Br_3SnMn(CO)_5$	+1.58	1.54	133
$Ph_2BrSnFe(CO)_2cp$	-2.42	2.52	142
$PhBr_2SnFe(CO)_2cp$	+2.72	2.65	142
$Br_3SnFe(CO)_2cp$	+2.16	1.63	142
$Br_3SnFe(CO)_2cp$	+1.82	1.60	133

(Table 3-3 cont'd)

b) Some other tin-manganese and tin-iron systems:

Compound	Q.S. calc[a]	|Q.S.| obs	Reference
$Cl_2Sn[Mn(CO)_5]_2$	2.24	2.10	143
$ClSn[Mn(CO)_5]_3$	-1.94	1.55	128
	-1.56	1.55	133
	-1.58	1.55	117
$Br_2Sn[Mn(CO)_5]_2$	2.24	2.12	143
$Cl_2Sn[Fe(CO)_2cp]_2$	2.50	2.39	131
	2.08	2.38	133
$Br_2Sn[Fe(CO)_2cp]_2$	2.50	2.42	143
	2.10	2.42	117
$ClSn[Mn(CO)_5][Fe(CO)_2cp]_2$	-2.10	2.02	127
$Me_3SnFe(CO)_2cp$	-0.58	0.46	114
$Me_3SnMn(CO)_5$		0.82[c]	143
$Me_2Sn[Mn(CO)_5]_2$	0.92	0.92	124
	1.34	0.92	117
$MeSn[Mn(CO)_5]_3$	+0.80	0.95	124
	+1.16	0.95	117
$Me_2ClSnMn(CO)_5$	-2.59	-2.60[b]	143
$MeCl_2SnMn(CO)_5$	+2.79	+2.62[b]	142
$(NCS)_2Sn[Fe(CO)_2cp]_2$	2.59	2.56	117
$(HCO_2)_2Sn[Fe(CO)_2cp]_2$	1.69	2.19	117
$(MeCO_2)_2Sn[Fe(CO)_2cp]_2$	1.76	2.60	117
$(MeCO_2)_3SnFe(CO)_2cp$	+1.52	1.87	117

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a) Sign given, except for $\eta = 1$, where the sign is indeterminant

b) Sign determined in reference 143

c) Value used to determine p.q.s. of $Mn(CO)_5$

Table 3-4

Bond Angle Data for Some Tin Transition Metal Systems

Compound	X-Sn-M[a]	R-Sn-X	Reference
$Ph_3SnMn(CO)_5$	112.7	106.0	134
$Ph_3SnFe(CO)_2cp$	113.4	105.2	135
$Cl_3SnFe(CO)_2cp$	119.2	98.3	136
$Br_3SnFe(CO)_2cp$	118	100	138
$PhCl_2SnFe(CO)_2cp$	129.7[b](114.4)[c]	99.7	137
Ph_3SnCl	106.4[d]	112.4[e]	154
Ph_2SnCl_2	100[f]	125.5[g]	150
$Ph_2Sn[Mn(CO)_5]_2$	117	100	152
$Ph_2Sn[Fe(CO)_2cp]_2$	116	95	154
$Me_2Sn[Fe(CO)_2cp]_2$	123	104	154
$Cl_2Sn[Fe(CO)_2cp]_2$	128.6	94.1	153

a) Average bond angles
b) C-Sn-Fe c) Cl-Sn-Fe d) Cl-Sn-C e) C-Sn-C
f) Cl-Sn-Cl g) C-Sn-C

s characters is not possible.

8) Iron Mossbauer - Results and Discussion

The formal oxidation state of the iron atom in molecules containing a Group IVB-iron bond can be considered as either iron(II) in which case the tin atom is also in the +2 oxidation state, or as iron (0). The oxidation state of tin is, in the latter case tin(IV) and since the entire tin Mossbauer results were explained assuming that tin was in the +4 oxidation state, the iron should be considered as iron(0). However as has been pointed out (129), the concept of oxidation state is very empirical, has little physical signficance, and is particularly confusing when applied to metal-metal bonded systems. Although there has been an enormous number of Mossbauer parameters reported for iron(0) compounds, and iron cyclopentadienyl compounds (34) there have been comparatively few successful attempts to correlate the trends in both the quadrupole splitting and centre shift values. The variation of quadrupole splitting with coordination number has been noted for some compounds (34), but those for fairly similar types of compounds have not proved to be ameanable to any qualitative or quantitative treatment. This is probably due to a large and variable $q_{valence}$ term, and to the great variation in and relative energies of the ligand and atomic orbitals from compound to compound.

For compounds containing a metal-iron bond the quadrupole splitting is insensitive to changes in metal or ligands. Even if the iron atom was considered to be in the +2 oxidation state, the p.q.s. treatment developed by Fitzsimmons (155) and Bancroft (118, 121) would still not apply. This is because of the obvious effect on the

bonding properties of both the carbonyl and cyclopentadienyl groups according to the nature of the metal and ligands as evidenced by a shift in the carbonyl stretching frequency and in the proton N.M.R. The practically non-existent trend in the quadrupole splitting data suggests that the iron atom is acting as a charge sink and is adopting essentially the same charge density and orbital imbalance in all the compounds studied.

The centre shifts for iron(0) compounds have been expressed as a sum of partial centre shifts (p.c.s.) (156) and similar to the theory successfully used for iron(II) compounds (118). However, from some more recent work on some carbonyl compounds that must be considered as iron(II), (157) the p.c.s. treatment is not always very successful due to the changing bonding properties of the carbonyl and cyclopentadienyl groups and hence in their p.c.s. values. Thus for iron(0) compounds and iron(II) compounds that contain carbonyl and cyclopentadienyl groups, the additivity rule breaks down because these groups draw off excess charge from the iron atom, and will consequently vary the p.c.s. value according to this loss of charge. However, the total centre shift, for iron(0) compounds will vary as the σ and π bonding abilities of the ligands. It is currently popular to consider the cyclopentadienyl group as a tridentate ligand, in which case the iron has formal octahedral symmetry. Thus an increase in σ donating power will result in an increased population of the iron d^2sp^3 hybrid orbital, and as the centre shift is more dependent upon s rather than p or d character , a decrease in the centre shift will result. The greater the π acceptor properties of the ligand, the greater will be

the delocalisation of the t_2g electrons. This will tend to decrease the shielding of the s electrons and hence decrease the centre shift. Thus the C.S. values will vary as the $-(\sigma + \pi)$ characteristics of the ligand.

For the compounds listed in Table 3-5, the C.S. values for compounds containing the same ligands increase in the order Si<Ge<Sn<Pb i.e. silicon can be considered as a stronger σ donor or π acceptor relative to tin. For a given metal the order of increasing $-(\sigma + \pi)$ bonding ability for the ligands increases in the order $Cl > C_6F_5 > Ph$ i.e. Cl_3M compounds have the highest centre shift values. Therefore, upon combining the two series, the Ph_3Si group can be considered as a strong σ donor relative to the Cl_3Sn group which is best considered as both a strong σ donor and π acceptor. However this effect is so very small that the series $Ph_{3-n}(C_6F_5)_nSnFe(CO)_2cp$ has an effectively constant centre shift. This makes any further comparison between the compounds not very meaningful since the σ and π effects are not easily separated.

9) Substituted Compounds - Results and Discussion

Previous work on the system $R_3SnFe(CO)(cp)L$ (R = Me, Ph or Cl, and L = CO, phosphine, phosphite, arsine, or stibine) and $R_3SnFe(cp)L_2$ (R = Me or Ph and L = phosphine or stibine) (114) indicates that the replacement of a carbonyl group by a weaker π acceptor group L causes the s density on the iron and tin atom to decrease and increase respectively. This is the reverse of what might be expected to happen if there was appreciable π bonding between the two metals. In this case, the effect of replacing CO by L would then decrease the

Table 3-5

Fe Mossbauer Data at 298°K[a]

Compound	C.S. mm/s[b]	Q.S. mm/s[b]
$Ph_3SiFe(CO)_2cp$	0.22	1.80
$Ph_3GeFe(CO)_2cp$	0.27	1.78
$Ph_3SnFe(CO)_2cp$	0.29	1.78
	0.35[c]	1.82[c]
	0.37[d]	1.83[d]
$Ph_3PbFe(CO)_2cp$	0.33	1.69
$(C_6F_5)_3SiFe(CO)_2cp$	0.23	1.82
$(C_6F_5)_3GeFe(CO)_2cp$	0.30	1.80
$(C_6F_5)_3SnFe(CO)_2cp$	0.31	1.81
$Ph(C_6F_5)_2SnFe(CO)_2cp$	0.29	1.77
$Ph_2(C_6F_5)SnFe(CO)_2cp$	0.31	1.70
$Cl_3SiFe(CO)_2cp$	0.20	1.91
$Cl_3Ge\ Fe(CO)_2cp$	0.22	1.76
$Cl_3SnFe(CO)_2cp$	0.33	1.81
	0.39[c]	1.84[c]
	0.40[d]	1.86[d]

a) C.S. values relative to $Na_2[Fe(CN)_5NO].2H_2O$
b) Uncomputed spectra; errors are ±0.02 mm/s and all line widths about 0.25 mm/s
c) Reference 114 at 80°K
d) Reference 123 at 80°K

π interaction between the metal atoms, and allow a greater amount of d density to be donated from the iron to the tin thereby increasing the s density on the iron atom and hence decreasing its centre shift. The effect of increasing the d density on the tin atom would then be to decrease its s density and also its centre shift. The results for the system $Ph_{3-n}Cl_nSnFe(CO)_{2-x}(cp)Lx$ (n = 0 to 3 for x = 1 and L = PPh_3, $P(OPh)_3$ and PEt_3; x = 2 for L = $P(OPh)_3$ and n = 3 x = 1 for $P(OEt)_3$) indicate that the previous observations are substantially correct, but the interpretation given in this work is somewhat different.

The ^{57}Fe Mossbauer results given in Table 3-6 show a net increase in s density at the iron atom in the order,

$P(OPh_3)_3 < PEt_3 < PPh_3 < P(OPh)_3 < P(OEt)_3 < CO$. This order is essentially the same as that found by Cullen et al in which the increase in s electron density was in the order phosphines<phosphites<CO, and that amongst the Group V elements themselves the order was Sb<As<P. They interpreted this to mean that the relative ability of the ligands to act as π acceptors was greatest for CO and least for stibines. The iron centre shifts are, however, a measure of both σ and π bonding ability and it is therefore incorrect to rank the ligands simply according to π back-donation alone. For the system described in this work the relative insensitivity of the iron to changes in the ligands bonding to tin is exemplified by the very small changes in centre shift, and the almost constant increase of this value upon replacement of a carbonyl group with a ligand L.

The tin centre shifts given in Table 3-7 also show an increase from the parent dicarbonyl compounds but the increase for a given ligand L is not very constant. However, the order of increase in s

density around the tin is CO<phosphites<phosphines<bisphosphites, and the similarity of this to the order of decreasing s density observed for the iron atom suggests that a synergic mechanism is operating in the tin-iron bond. An increase in s density in the tin-iron bond will lead to a decrease in s density in the tin-carbon bond and this can be followed by measuring the change in the Sn-C-H coupling constant in the P.M.R. spectra. The results for the system $Me_3SnFe(CO)(cp)L$ show that this decrease exactly parallels the order in the iron centre shift (114). For a given ligand L the positive increase in centre shift indicates an increase in s character of the Sn-Fe bond by an amount that is proportional to the $-(\sigma + \pi)$ bonding characteristics of the ligand i.e. increases in the order, CO<phosphites<phosphines<biphosphites.

The variation of the quadrupole splitting with a ligand L is however not easy to explain. The p.q.s. parameters for $Fe(CO)_2(cp)L$ given in Table 3-8 are derived from the observed quadrupole splittings for the $Ph_3SnFe(CO)(cp)L$ species and found to be all approximately equal, but less than that for $Fe(CO)_2cp$ i.e. the group Fe(CO)(cp)L is a poorer p donor than $Fe(CO)_2cp$ and about the same as $Mn(CO)_5$. The quadrupole splitting for the triphenyltin compounds should then increase by an amount equal to twice the difference between the p.q.s. values for $Fe(CO)_2cp$ and Fe(CO)(cp)L, but at the same time decrease by the same amount for the trichlorotin species. The fact that this is not observed (Table 3-7) suggests that either the distortions in the molecular geometry of the Cl_3Sn species are enough to raise the observed value for the quadrupole splitting, and hence obscure the

predicted trend, or that the p.q.s. values for the Fe(CO)(cp)L species are not particularly accurate. Indeed, the calculated values for the quadrupole splitting for the diphenylchlorotin and phenyldichlorotin species are effectively independent of the nature of L regardless of whether the p.q.s. value was calculated from the triphenyltin or trichlorotin compounds. The greater distortion in the latter compounds ought to give a larger experimental quadrupole splitting and hence a larger p.q.s. value for Fe(CO)Lcp. In fact, the largest difference in the p.q.s. value for any one type of Fe(CO)(cp)L species was only slightly smaller than the total variation for all the Fe(CO)(cp)L species, so that it is impossible to infer any differences in the p donor strengths of the Fe(CO)(cp)L groups from inspection of the p.q.s. values alone.

The rather small changes in both the centre shift and quadrupole splittings encountered in this work are rather disappointing but are probably due to the essential similarity of the ligands used. It is also possible that part of this insensitivity arises as a result of the position of substitution. A ligand that is substituted trans to the metal-metal bond will be expected to exert a greater effect on the electronic environment of this bond that which is substituted cis, as in this case. However in the compounds $R_3SnMn(CO)_4PPh_3$ (R = Ph or Cl) and $PhClSn[Co(CO)_4][Co(CO)_3PPh_3]$, where the ligand PPh_3 is substituted trans to the Sn-Mn and Sn-Co bonds respectively, the increase in C.S. of these compounds relative to the unsubstituted derivatives is of the same order of magnitude as that reported in this work.

Since π bonding in the metal-metal bond is thought to be more important for the Cl_3Sn species than for the Ph_3Sn species the increase in the C.S. value for the latter species, relative to the unsubstituted compound ought to be larger than for the trichlorotin species. Since a positive but constant increase in C.S. is always observed between the substituted and unsubstituted derivatives this suggests that the amount of π bonding in the Sn-Fe bond is quite small or is of equal importance in both the triphenyltin and trichlorotin species. The substitution of a weakly bonding fluorocarbon derivative of Group V (114), still causes a small increase in the s character of the metal-metal bond, whereas if π bonding was important then the change in the electronic environment of the Sn-Fe bond would be expected to become more apparent in this case.

In conclusion, it appears that the substitution of CO by a Group V ligand has only a minimal effect on the electronic environment of the metal-metal bond,and is very insensitive both to the nature and position of substitution of the ligand. Although the tin Mossbauer spectra need not be interpreted in terms of π effects, the existance of π bonding in the metal-metal bond cannot be ruled out; but if it is present at all, its effect on the nature of the metal-metal bond is probably quite small.

Table 3-6

^{57}Fe Mossbauer Data for the Compounds $Ph_{3-n}Cl_nSnFe(CO)_{2-x}(cp)L_x$

		at 298°K				
		[a] C.S. mm/s	Δ(CS) [b,c]	Q.S. mm/s	Γ_1	Γ_2
x = 0	$Ph_3SnFe(CO)_2cp$	0.28		1.75	0.27	0.26
	$Ph_2ClSnFe(CO)_2cp$	0.30		1.71	0.25	0.28
	$PhCl_2SnFe(CO)_2cp$	0.30		1.68	0.25	0.27
	$Cl_3SnFe(CO)_2cp$	0.32		1.82	0.27	0.26
x = 1 L=PPh_3	$Ph_3SnFe(CO)cpPPh_3$	0.39	0.11	1.79	0.23	0.25
	$Ph_2ClSnFe(CO)cpPPh_3$	0.39	0.09	1.73	0.24	0.24
	$PhCl_2SnFe(CO)cpPPh_3$	0.40	0.10	1.73	0.24	0.24
	$Cl_3SnFe(CO)cpPPh_3$	0.41	0.09	1.80	0.24	0.25
	$Cl_3SnFe(CO)cpPPh_3$	0.41	0.09	1.80	0.24	0.25
	$Cl_3SnFe(CO)cpPEt_3$	0.40	0.08	1.84	0.30	0.31
	$Cl_3SnFe(CO)cpP(OPh)_3$	0.36	0.04	1.77	0.25	0.26
	$Cl_3SnFe(CO)cpP(OEt)_3$	0.35	0.03	1.79	0.30	0.26
x = 2 L=$P(OPh)_3$	$Cl_3SnFecp[P(OPh)_3]_2$	0.44	0.12	1.80	0.25	0.26

a) C.S. relative to sodium nitroprusside
b) ΔC.S. = C.S.$[R_3SnFe(CO)(cp)L]$ - C.S.$[R_3SnFe(CO)_2cp]$
c) errors estimated to be ±0.1 mm/s

Table 3-7

^{119}Sn Mossbauer Parameters for the System $Ph_{3-n}Cl_nSnFe(CO)_{2-x}(cp)L_x$

		at 80°K					
	Compound	C.S.	ΔC.S.[a]	Q.S.	ΔQ.S.[b]	Γ_1	Γ_2 (mm/s)
x = 1	$Ph_3SnFe(CO)cpPPh_3$[c]	1.53	0.14	0.66	0.34	1.22	0.95
	$Ph_2ClSnFe(CO)cpPPh_3$	1.63	0.11	2.74	0.20	1.07	1.07
	$PhCl_2SnFe(CO)cpPPh_3$	1.80	0.10	3.00	0.16	1.04	1.05
	$Cl_3SnFe(CO)cpPPh_3$[c]	1.86	0.11	1.89	0.06	1.10	1.04
	$Ph_3SnFe(CO)cpPEt_3$	1.51	0.12	0.86	0.54	1.03	1.00
	$Ph_2ClSnFe(CO)cpPEt_3$	1.63	0.11	2.59	0.05	1.27	1.08
	$PhCl_2SnFe(CO)cpPEt_3$	1.83	0.13	3.03	0.19	1.23	1.11
	$Cl_3SnFe(CO)cpPEt_3$	1.95	0.20	1.91	0.08	1.15	1.07
	$Ph_3SnFe(CO)cpP(OPh)_3$	1.48	0.09	0.53	0.21	0.97	0.97[d]
		1.39	0	0	-	1.29	
	$Ph_2ClSnFe(CO)cpP(OPh)_3$	1.57	0.05	2.69	0.15	1.29	1.13
	$PhCl_2SnFe(CO)cpP(OPh)_3$	1.77	0.07	2.83	-0.01	1.13	0.98
	$Cl_3SnFe(CO)cpP(OPh)_3$	1.79	0.04	1.82	-0.01	1.14	0.96
X = 2	$Ph_3SnFe(cp)[P(OPh)_3]_2$	1.49	0.10	0.78	0.46	1.05	0.93
	$Ph_2ClSnFe(cp)[P(OPh)_3]_2$	1.65	0.13	2.71	0.17	1.07	1.03
	$PhCl_2SnFe(cp)[P(OPh)_3]_2$	1.75	0.05	2.90	0.06	1.07	1.04
	$Cl_3SnFe(cp)[P(OPh)_3]_2$	1.83	0.13	1.92	0.09	1.17	0.97
x = 1	$Cl_3SnFe(CO)cpP(OEt)_3$	1.77	0.02	1.85	0.02	1.12	1.04

a) $\Delta C.S. = C.S.[R_3SnFe(CO)(cp)L] - C.S.[R_3SnFe(CO)_2cp]$
b) $\Delta Q.S. = Q.S.[R_3SnFe(CO)(cp)L] - Q.S.[R_3SnFe(CO)_2cp]$

errors for both are twice the errors in C.S. and Q.S. i.e. about 0.04 mm/s

c) From reference 114, $Ph_3SnFe(CO)(cp)PPh_3$, C.S. = 1.48; Q.S. = 0.69 mm/s, and $Cl_3SnFe(CO)cpPPh_3$, C.S. = 1.86; Q.S. = 1.88 mm/s
d) constrained fit, line widths held at 0.97 mm/s

Table 3-8

Partial Quadrupole Splitting Values for the $Fe(CO)_{2-x}(cp)Lx$ Moiety

	L	p.q.s.	mm/s
x = 1	CO	-1.08	
	PPh_3	-0.95[a]	-0.91[b]
	PEt_3	-0.96	-0.83
	$P(OPh)_3$	-0.91	-0.99
	$P(OEt)_3$	-0.93	---
x = 2	$P(OPh)_3$	-0.96	-0.87

Values calculated using - Q.S. = $2p.q.s.(R) + 2p.q.s.\left[Fe(CO)(cp)L\right]$

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a) Calculated from compounds of the type $Cl_3SnFe(CO)(cp)L$ taking the p.q.s. for Cl to be zero

b) Calculated from compounds of the type $Ph_3SnFe(CO)(cp)L$ taking the p.q.s. for Ph to be -1.26 mm/s

Table 3-9

Predicted and Observed Values of the Quadrupole Splitting

Compound	Q.S. obs	p.q.s. of iron species	Q.S. calc	η	Q.S. av.
$Ph_3SnFe(CO)(cp)PPh_3$	0.66	--	--	0	
$Ph_2ClSnFe(CO)(cp)PPh_3$	2.74	-0.95	-2.39	0.34	-2.39
		-0.91	-2.38	0.39	
$PhCl_2SnFe(CO)(cp)PPh_3$	3.00	-0.95	+2.60	0.93	+2.59
		-0.91	+2.57	0.90	
$Cl_3SnFe(CO)(cp)PPh_3$	1.89	-0.91	-1.82	0	
$Ph_3SnFe(CO)(cp)PEt_3$	0.86	--	--	0	
$Ph_2ClSnFe(CO)(cp)PEt_3$	2.59	-0.96	-2.39	0.33	-2.38
		-0.83	-2.37	0.44	
$PhCl_2SnFe(CO)(cp)PEt_3$	3.03	-0.96	+2.61	0.93	+2.57
		-0.83	+2.53	0.88	
$Cl_3SnFe(CO)(cp)PEt_3$	1.91	-0.83	+1.86	0	
$Ph_3SnFe(CO)(cp)P(OPh)_3$	0.53	--	--	0	
$Ph_2ClSnFe(CO)(cp)P(OPh)_3$	2.69	-0.91	-2.38	0.39	-2.38
		-0.99	-2.39	0.30	
$PhCl_2SnFe(CO)(cp)P(OPh)_3$	2.83	-0.91	+2.57	0.90	+2.60
		-0.99	+2.63	0.95	
$Cl_3SnFe(CO)(cp)P(OPh)_3$	1.82	-0.99	+1.98	0	
$Ph_3SnFe(cp)[P(OPh)_3]_2$	0.78	--	--	0	
$Ph_2ClSnFe(cp)[P(OPh)_3]_2$	2.71	0.96	-2.39	0.33	-2.38
		0.87	-2.38	0.43	
$PhCl_2SnFe(cp)[P(OPh)_3]_2$	2.90	0.96	+2.61	0.93	+2.58
		0.87	+2.54	0.88	
$Cl_3SnFe(cp)[P(OPh)_3]_2$	1.92	0.87	+1.74	0	

CHAPTER 4

MASS SPECTROMETRY

1) Introduction

During the last seven years, mass spectrometric studies on organometallic systems have become so widespread that today it can be considered to be a field in its own right. However, since there are many more problems associated with the mass spectra of organometallics than with organic compounds, special precautions are necessary to avoid difficulties in the interpretation of the data, and serious errors in the measurement of appearance potentials.

The use of very high temperatures to volatalise the sample or heat the ion source must, where possible be avoided, since organometallic compounds have a pronounced tendency to undergo thermally induced decomposition rearrangement or polymerisation reactions (159 - 161) in the sampling system or ion source. The extent to which these effects occur is difficult to estimate since they may be more pronounced in the gas phase, even at moderately low temperatures, than those found from normal pyrolysis studies. Quite often the heat developed by the filament alone is enough to raise the temperature of the surrounding metal parts such that a collision of a molecule with this surface may cause partial pyrolysis. Most organometallic compounds pyrolyse to give a thin conducting metallic film which covers the entire inside surface of the ion source, such that it can act as

a catalyst for the thermal decomposition of other molecules and eventually causes the ion source to short-circuit. In addition the species formed from the pyrolysis of such molecules will have an almost equal probability of ionisation as any other molecules and thus could severely contaminate or obscure the mass spectrum of the molecule under investigation.

The extent to which possible pyrolysis can occur is however more important if appearance potential data is to be used to obtain an estimate of bond strengths. Since the appearance potential of an ion is defined as the least amount of energy needed to form that ion, the validity of the measurement will depend upon the correct assignment of the process involved in the threshold measurement. Successive collisions of an ion or molecule with the walls of the spectrometer may not only lead to decomposition, but also to an increase in the population of the next lowest lying vibrational or even electronic levels so that different fragmentation patterns and low values for the appearance potentials may result for these ions over those in the unexcited state (162 - 165).

Even though there have been several attempts to minimise unwanted thermal effects by use of cold ion sources (44), chopped molecular beams (166), or photoionisation (167) methods these involve either costly or specially constructed instruments. Despite the difficulties encountered with the more conventional types of spectrometer a large amount of information can be gathered if the compounds under study are carefully chosen. Compounds that form a well defined series are particularly suitable for study, since within

such a series, unusual thermal effects that may only be present in one compound can be readily identified by comparison with its congeners. Compounds that undergo ready thermal decomposition or are easily attached by the background water vapour, or oxygen,which are always present in commercial machines, are generally unsuitable for study since it is almost impossible to determine if the ions in the mass spectra arise from the molecular ion or from the ions formed by oxidation or hydrolysis of the compound before primary ionisation takes place.

The mass spectra of organometallic compounds have been used to determine 1) the molecular weight 2) the characteristic fragmentation patter and 3) specific indications of the strength of certain bonds.

The polyisotopic nature of all but twenty of the elements likely to be encountered can give valuable information as to the identity of an ion,but when two or more polyisotopic patterns overlap, as for some metal hydrides (168), interpretations of the pattern is made more difficult. It is generally assumed, though not always true, that the peak or group of peaks appearing at the highest mass to charge ratio is due to the parent (or molecular) ion, but in cases where no parent ion is visible, the identity of the compound and hence its molecular weight can sometimes be deduced from a detailed examination of the remainder of the spectrum. Detailed studies of the fragmentation patterns of a series of compounds show that of all the possible processes that can occur, only a relatively small number are actually observed. The relative abundances of these ions give some indication of their stability and, although due to possible valency

changes, it is not always possible to write specific structures for such ions, the one drawn is often that which would be expected to be the most stable. Information concerning the modes of fragmentation is derived by the analysis of the metastable peaks. In fact changes in the type of transition observed are the only real evidence for a change in the relative bond strength from one compound to another, since the abundances of the ions themselves cannot be used to indicate such a change. The ion abundances are a measure of the probability of ionisation of that particular species and are consequently a measure of the relative rate of formation and of its relative stability. However, although it is extremely tempting to relate ion abundances to the expected variation in bond strength, this will, in most cases, give very misleading values for the relative bond strengths.

Metastable ions arise from the breakdown of fragment ions during their passage through the instrument. The lifetimes of these ions must be such that although some of them will reach the analyser and will thus be recorded at a normal peak at a single nominal mass, many of them will dissociate in the field free region between the magnetic field and analyser and will be recorded as diffuse low intensity peaks at non-integral masses. The intensity of these peaks is related to the probability of the transition from which it arises, and should, if there is no great loss of kinetic energy during the decomposition, have the same appearance potential as the parent fragment ion. Thus in certain cases the measurement of these appearance potentials provides a check on the assignment of the transition.

However, the observance of metastable peaks depends upon the geometry

of the system and on the slit widths used. For most instruments the slits must be opened such that a loss of resolution cannot be avoided, but in order to achieve a reasonable correlation of the bonding in a compound with its fragmentation pattern as many metastable ions as possible must be observed. Thus in some cases where the metastable ions are extremely weak, spectra at very high gain must be obtained. This unfortunately causes the base line to lift when there are groups of peaks spaced very closely together such that the metastable peak is buried and is not easily seen.

For the A.E.I. MS-12 used in this work, a parent fragment ion m_1, breaking down to another ion m_2, and an uncharged or radical species of mass $(m_1 - m_2)$, will give a metastable peak m^* at the value of m_2^2/m_1. Very often several metastable transitions will form a sequence that connect all the important ions in the spectra, but although a certain transition has been found it does not necessarily follow that the process occurs in a single step. Thus no inference must be placed on the structure of the radical species lost, since these would be comprised of two or more radicals that are not necessarily bonded together. However the most favoured processes are normally those which involve the loss of a neutral species. The shape of the metastable ion depends upon the position of dissociation in the instrument, the stability of the daughter ion and the kinetic energy involved in the dissociation. However, the shape of many metastable ions found in the spectra of polyiostopic compounds (38) frequently, though not always, is the same as the parent fragment ion from which it is derived and thus often falicitates the assignment of such transitions.

The study of appearance and ionisation potentials of similar

ions produced from similar molecules, can give a very approximate indication of certain bond strengths, but although a large number of transition metal carbonyls (36 - 37) have been studied there has been little correlation of these values with bond strengths due to the lack of the necessary thermodynamic data. In addition, the ionisation potentials (I.P.) of organometallic species (40, 169) show an enormous variation in their literature values due to the sensitivities of these values to the source temperatures, and the fact that the desired ion may be produced either very inefficiently or by several concurrent processes.

If a molecule AB is ionised according to

$$AB + e \rightarrow A^+ + B + 2e$$

and there is no excess kinetic energy involved, then the appearance potential (A.P.) of A^+ is given by,

$$AP(A)^+ = D(A - B) + IP(A)^+$$

$$= \Delta H_{reaction} = \Delta H_f^o(A^+) + \Delta H_f^o(B\ ) - \Delta H_f^o(AB)$$

where D(A - B) is the dissociation energy of the AB bond, $IP(A^+)$ is the ionisation potential of the ion A^+ and ΔH_f^o refers to the standard heats of formation of the ion A^+, the radical B and the neutral species AB in the gas phase.

Similarly, the ionic bond dissociation energy $D(A - B)^+$ is given by:

$$D(A - B^+) = A.P.(A^+) - IP(A - B)$$

Although the appearance potential of any reasonably abundant ion is relatively easy to measure, the ionisation potential of this species can only be effectively measured by the direct gas phase ionisation

of the free radical, (39, 44) since there is rarely enough reliable thermodynamic data available for this to be calculated on the basis of appearance potentials. In addition it is well known that in compounds containing several chemically equivalent bonds, the average bond dissociation energy is always less than the energy needed to break the firstbond, so that in order to calculate any one of these quantities an empirical and rather arbitrary relationship between the two is needed (44).

Whether the ion is produced by electron impact of a compound or by ionisation of the free radical produced by the thermal decompositon of suitable derivatives, the appearance potential cannot be taken at the point where the signal for the ion first appears. Factors such as the signal to noise ratio of the analyser, the non monoenergetic nature of the electron beam, space charge effects, contact potentials and interfering stray magnetic fields produce a 'foot' or 'tail' in the ionisation efficiency curve such that it asymptotically approaches the energy axis at the threshold voltage. Since the energy scale may vary between instruments, it is important that the energy scale be calibrated by the use of an inert gas of accurately known appearance potential at the same time as the other determinations are made. The calibrant is normally a noble gas since in this case the ionisation potential equals the appearance potential, but its choice must be made so that the ions produced from the calibrant gas do not overlap with the ions whose appearance potential is to be measured.

Several methods have been used to determine appearance potentials (170), but the most popular is that due to Warren (171). In this

method, the partial pressures of the calibrant gas and the sample are adjusted so that the abundances of any given peak in the ions under study are the same at 50 ev. Starting below the expected appearance potential (i.e. ca. 5 ev) a plot is then made of the ion current versus the electron energy for each ion in the region of 0.1 to 1% of the 50 ev ion current. The linear portions of the ionisation efficiency curves thus obtained are adjusted to be parallel to each other by the multiplication of either curve by a suitable amount. The voltage differences between the two curves are then plotted against various small values of the ion current and linearly extrapolated to zero ion current. The intercept on the electron energy axis is then added to the known appearance potential of the calibrant to give the appearance potential of the sample ion.

Due to the fact that the ion is assumed to form in its first excited state, and that there is no excess kinetic or excitational energy involved, the ionisation potentials determined in this way represent the upper limit of the values determined by other methods, and may give higher values for the bond dissociation energy.

2) The Mass Spectra of Organometallic Compounds

The mass spectra of some metal carbonyls and their derivatives have been reviewed by Lewis and Johnson (35) and reviews of the whole organometallic field in general have been provided by Bruce (36), Cais and Lupin (37) and by Glockling, Chambers and Light (38). Although a very large number of metal-metal bonded derivatives have been examined, these have been chosen in a rather haphazard manner, and except for some polynuclear carbonyls and their simpler derivatives

(172 - 179) there has been little attempt to correlate the change in the spectra with a systematic change of any one variable at a time. This approach is important if the observed features are to be rationalised and has been found to be particularly effective for a large variety of organometallic derivatives of Groups III (180), IV (38, 181 - 183), V (184 - 186), and VI (187).

Despite the current activity in this area only a relatively small number of mass spectral studies on the compounds containing a single Group IV-transition metal bond have been reported. These include, $Me_3MMn(CO)_5$ (44), $Me_3MM'(CO)_3cp$ (M = a Group IV metal, and M' = Cr, Mo or W) (41) $R_3GeM'(CO)_3cp$ (R = Me, Et or n-Pr and M' = Mo or W) (189) $R_3SiCo(CO)_4$ (R_3 = Cl_3, F_3, Me_3, and MeF_2) (190), $Me_3SnCo(CO)_4$ (191), $Ph_{3-n}Cl_nSnFe(CO)_2cp$ (n = 0 to 3) (51), $Ph_3SnMn(CO)_5$ (192, 193), $PhBr_2SnMn(CO)_5$ (192) $Me_3SnMo(CO)_3cp$ (191) and $Ph_3SnFe(CO)_2cp$ (172). Their spectra, and those of metal-metal bonded compounds in general, are characterised by the low abundance of the molecular ions, the stepwise loss of CO, the general weakness of the metal-metal bond and the migration of organic groups to the other metal atom. In nearly all cases the number of metastable transitions used to support the fragmentation scheme is very small due either to the fact that they were not observed or were not reported. In the absence of this data, it is difficult to arrive at reliable conclusions concerning the relative bond strengths.

The introduction of a polyhalo organic group into the compound produces another characteristic feature in the mass spectrum. This is the migration of the halogen from the carbon atom to the more

electropositive metal, which is normally eliminated as a metal halide species. This process has been well established in the mass spectra of nearly all fluorocarbon derivatives (36, 181 - 183, 185) by the observance of the appropriate metastable ions. For polychlorinated derivatives, although metal chloride ions are still observed (183, 193), the assignment of the appropriate transitions are made more difficult by the polisotopic nature of a compound containing several chlorine atoms. This causes a large range in mass for a given single ion such that the metastable transitions are considerably broadened and may be buried under the base line.

Metal fluoride eliminations do not normally take place from the molecular ion, but from the ion resulting from the loss of one or two organic groups. The fragmentation normally takes place in such a way that the charge is left on the residual part of the molecule, and the metal fluoride is eliminated as a neutral or radical species, although its elimination as an ion has been observed (182, 35, 36). For perfluoroaromatic compounds, the elimination of a metal fluoride species can lead to fluorocarbon ions that conceivably have ring structures analogous to those of bi or triphenylenes (181, 182, 185). When hydrogen is also present in the compound loss of HF is also a common process (36, 185), but in general the fragmentation pattern of the fluorocarbon derivatives bear practically no resemblance at all to their hydrocarbon analogies (183, 185).

Two mechanisms for the migration of fluorine from the aromatic ring to the metal atom have been proposed. The first of these is that whenever there are unsaturated or σ-bonded ligands present,

these become π-bonded to the metal during the fragmentation, and this hypothesis is supported by the extent of fluorine migration observed for the ortho, meta and para complexes of $FC_6H_4Mn(CO)_5$ (192, 194). There is only a small difference in the abundances of the MnF^+ ions for each of these three compounds but ortho migration seems to be preferred. The second theory is that the non-bonding orbital on the fluorine atom interacts with the vacant d orbital on the metal and the fluorine is transferred via a three-centre bond (195,196). This theory adequately explains why no fluorine migration is observed for the fluorinated derivatives of some aromatic amines (195), ethers (181, 186) and alcohols (181) since these compounds lack the appropriate d orbitals; but it does not explain the absence of fluorine migration in some perfluorinated hetocyclic derivatives of Group VI (188), or the extensive loss of boron fluoride species observed in the mass spectrum of $(C_6F_5)_3B$ (197).

Thus the mechanism of fluorine migration is by no means settled; nor is the mechanism by which the entire organic group migrates to the other metal atom. This latter process could arise by the scrambling of the organic group just after primary ionisation has taken place, or during the fragmentation of the molecule. This is possibly aided by the presence of d orbitals on the metal and by the creation of a vacant coordination site formed by the loss of one organic group (198).

Since neither of these mechanisms is proved, no attempt will be made to postulate mechanisms for the migration of fluorine or of the organic species in this thesis, since both of these could occur

by the complete scrambling of the substituents on the ring, and give rise to structures that bear no relation to those in the ground state.

3) Results and Discussion:

The $Ph_3MMn(CO)_5$ Derivatives

The ion abundances, expressed as a percentage of the total ion current, are shown in Table 4-1 and the proposed fragmentation schemes are shown in Figures 4-1 to 4-3.

The molecular ions are very low in abundance and except for the silicon derivative show no or extremely weak ($\leq 0.1\%$) ions resulting from the loss of one or more carbonyl groups from the molecular ion. The silicon and germanium derivatives did however show the appropriate metastable peaks for the loss of two carbonyl groups from $Ph_3SiMn(CO)_4^{+\cdot}$, and $Ph_3GeMn(CO)_2^{+\cdot}$ respectively

$$Ph_3SiMn(CO)_4^{+\cdot} \rightarrow Ph_3SiMn(CO)_2^{+\cdot} + 2CO \qquad m^* \text{ calc: } 321.5 \quad m^* \text{ found: } 322.0$$

$$Ph_3GeMn(CO)_2^{+\cdot} \rightarrow Ph_3GeMn^{+\cdot} + 2CO \qquad m^* \text{ calc: } 311.8 \quad m^* \text{ found: } 312.0$$

The silicon derivative showed ions that were due to the loss of one or three carbonyl groups from the molecular ion. In all cases the base peak was the Ph_3M^+ ion, and this was formed by either the loss of the $Mn(CO)_5$ radical directly, or by loss of all five carbonyl groups, and then manganese, from the parent ion. In most cases the appropriate metastable peaks for both transitions were observed.

			m* calc.	m* found
$Ph_3MMn(CO)_5^{+\cdot} \rightarrow Ph_3M^+ + Mn(CO)_5$	M = Si^{28}	147.8	148.0
	M = Sn^{120}	225.6	~225.0
	M = Pb^{208}	304.0	~304.0

		m* calc.	m* found
$Ph_3MMn^{+\cdot} \rightarrow Ph_3M^+ + Mn$	$M = Si^{28}$	213.6	213.5
	$M = Ge^{74}$	258.5	258.4
	$M = Sn^{120}$	303.5	303.5

The remainder of the spectra are dependent on the relative metal-carbon bond strengths, and do not appear to show any great variation in the metal-metal bond strength since in all cases cleavage of the metal-metal bond occurs at an early stage of fragmentation, and the spectra show few ions that contain more than one metal. A further indication of the insensitivity of the metal-metal bond to the fragmentation route is the almost constant abundances of the ion series $Mn(CO)_n^+$ (n = 0 to 5) throughout the series.

For the silicon derivative, initial fragmentation of the Ph_3M^+ ion is by loss of benzene (or by phenyl and a hydrogen radical) to give the ion $C_{12}H_9M^+$ which then undergoes further fragmentation by successive loss of acetylene to give the series of ions $C_{10}H_7Si^+$, $C_8H_5Si^+$, and $C_6H_3Si^+$.

	* calc	* found
$C_{12}H_9M^+ \rightarrow C_{10}H_7Si^+ + C_2H_2$	132.7	132.8
$C_{10}H_7Si^+ \rightarrow C_8H_5Si^+ + C_2H_2$	107.4	107.5
$C_8H_5Si^+ \rightarrow C_6H_3Si^+ + C_2H_2$	82.2	82.0

Similar, but less important losses of acetylene are also seen from the $C_{10}H_9Si^+$ ion to give the series of ions $C_8H_7{}^+Si$, $C_6H_5Si^+$, $C_4H_3Si^+$ and finally C_2HSi^+, but the origin of the $C_{10}H_9Si^+$ ion remains obscure, although it could arise by the elimination of the acetylene radical $C_2H\cdot$ from $Ph_2Si^{+\cdot}$.

	m* calc.	m* found
$C_{10}H_9Si^+ \rightarrow C_8H_7Si^+ + C_2H_2$	109.3	109.3
$C_8H_7Si^+ \rightarrow C_6H_5Si^+ + C_2H_2$	84.2	84.3
$C_6H_5Si^+ \rightarrow C_4H_3Si^+ + C_2H_2$	59.4	59.3

Another, but relatively minor fragmentation route for the Ph_3Si^+ ion is by the successive loss of one or two neutral molecules of hydrogen, and a similar loss of hydrogen from $PhSi^+$ is also observed.

	m* calc.	m* found
$Ph_3Si^+ \rightarrow C_{18}H_{11}Si^+ + H_2$	255.0	255.0
$Ph_3Si^+ \rightarrow C_{18}H_{11}Si^+ + 2H_2$	251.0	251.0
$C_{18}H_{11}Si^+ \rightarrow C_{18}H_9Si^+ + H_2$	251.1	251.0
$C_6H_5Si^+ \rightarrow C_6H_3Si^+ + H_2$	101.0	101.0

The loss of benzene from the Ph_3Si^+ ion was not supported by a metastable transiton, but the analogous transition was observed for the germanium compound, and further proof that such transitions are fairly common for both these derivatives was provided by the metastable supported loss of benzene from $Ph_2Si^{+\cdot}$,

	m* calc.	m* found
$Ph_2Si^{+\cdot} \rightarrow C_6H_4Si^{+\cdot} + C_6H_6$	59.4	59.3

Although the loss of acetylene or benzene is the predominant fragmentation pathway for these and other silicon derivatives (38), the loss of a hydrogen or phenyl radical can occur as evidenced by the formation of $(C_6H_4)_2Si^+$ by two separate routes,

	m* calc.	m* found
$Ph(C_6H_4)_2Si^+ \rightarrow (C_6H_4)_2Si^{+\cdot} + Ph$	126.0	126.0
$C_{12}H_9Si^+ \rightarrow (C_6H_4)_2Si^{+\cdot} + H$	179.0	179.0

For the germanium derivative, the loss of hydrogen or benzene can still occur from the ion Ph_3Ge^+,

	m* calc.	m* found
$Ph_3Ge^+ \rightarrow C_{18}H_{13}Ge^+ + H_2$	301.0	301
$Ph_3Ge^+ \rightarrow C_{12}H_9Ge^+ + C_6H_6$	168.9	169.0

but another equally important mode is the loss of biphenyl,

	m* calc.	m* found
$Ph_3Ge^+ \rightarrow PhGe^+ + Ph_2$	74.8	74.7

to give the ion $PhGe^+$, which then successfully loses acetylene to give the ions $C_4H_3Ge^+$ and finally C_2HGe^+.

	m* calc.	m* found
$PhGe^+ \rightarrow C_4H_3{}^+Ge + C_2H_2$	103.5	103.3

This does not occur with the rearrangement ion $PhMn^+$ since there is no ion due to $C_4H_3Mn^+$, and the appropriate metastable for the process

	m* calc.	m* found
$PhMn^{+\cdot} \rightarrow Mn^{+\cdot} + Ph$	22.9	22.8

was found to be very common in this and other spectra containing fairly large abundances of this ion. Similarly, when large peaks due to the phenyl ion are observed the metastable for the loss of acetylene from this is also seen,

	m* calc.	m* found
$C_6H_5^+ \rightarrow C_4H_3^+ + C_2H_2$	33.8	33.8

The mass spectrum of the tin compound has been reported previously (51, 192, 172) but although the identities and abundances of the ions are in fairly good agreement with those reported in this work, only a few metastable transitions were reported and no attempt

at a detailed examination was made.

Unlike the silicon and germanium derivatives, the tin compound shows no loss of hydrogen or benzene from the Ph_3Sn^+ ion, and the fragmentation of the $PhSn^+$ ion by loss of acetylene becomes rather unimportant. The controlling factor in the fragmentation of this and other tin compounds (38) is the cleavage of the tin-carbon bond. This can occur before the metal-metal bond is broken so that the $Ph_3SnMn^{+\cdot}$ ion can fragment to give the ions $PhSnMn^{+\cdot}$, or $PhSn^+$, as well as the ion Ph_3Sn^+ resulting from the loss of manganese.

	m* calc.	m* found
$Ph_3SnMn^{+\cdot} \rightarrow PhSnMn^{+\cdot} + Ph_2$	156.4	156.3
$Ph_3SnMn^{+\cdot} \rightarrow PhSn^+ + Ph_2Mn$	95.5	95.5

In common with the germanium derivative, and other triphenyltin derivatives, loss of diphenyl from the Ph_3Sn^+ ion is also observed.

	m* calc.	m* found
$Ph_3Sn^+ \rightarrow PhSn^+ + Ph_2$	110.5	110.5

However, there is little tendency for the ion $PhSn^+$ to lose acetylene, and the most favoured fragmentation is by loss of phenyl to give the tin ion.

	m* calc.	m* found
$PhSn^+ \rightarrow Sn^+ + Ph$	73.0	73.0

Although the loss of benzene is not common in these spectra, two metastable processes resulting in the formation of $C_4H_4^{+\cdot}$ and Ph^+ from the benzene ion were also found.

	m* calc.	m* found
$C_6H_6^{+\cdot} \rightarrow C_4H_4^{+\cdot} + C_2H_2$	34.7	34.7
$C_6H_6^{+\cdot} \rightarrow C_6H_5^{+} + H$	76.0	76.0

The decreasing strength of the metal-carbon bond as the group M becomes heavier is further exemplified by the lead derivative in which one of the phenyl groups is removed before all the carbonyls are lost, and gives rise to the series of ions $Ph_2PbMn(CO)_n^+$ (n = 0, 3, 4 and 5). A similar loss of a methyl group from the series $Me_3MMn(CO)_5$ is also known to occur (44) so that the abundance of the $Me_2MMn(CO)_5^+$ ion increases in the order Si<Ge<Sn<Pb and presumably reflects in part the decreasing Me-M bond strength. Although there were no metastable transitions for the loss of CO from the molecular ion, the simultaneous loss of two molecules of CO was seen from the ion $Ph_2PbMn(CO)_5^+$.

	m* calc.	m* found
$Ph_2PbMn(CO)_5^+ \rightarrow Ph_2PbMn(CO)_3^+ + 2CO$	450.6	450.5

The ion $Ph_3PbMn^{+\cdot}$ undergoes a rather unusual transition since it not only loses manganese, but it also loses lead to give the ion $Ph_3Mn^{+\cdot}$, which then further fragments to give the very abundant ion $PhMn^{+\cdot}$, and eventually Mn^+ by loss of a phenyl radical as previously described,

	m* calc.	m* found
$Ph_3PbMn^{+\cdot} \rightarrow Ph_3Mn^{+\cdot} + Pb$	165.6	165.7
$Ph_3Mn^{+\cdot} \rightarrow PhMn^{+\cdot} + Ph_2$	60.9	61.0

The $PhMn^{+\cdot}$ ions observed in the other spectra are of much lower abundance, and presumably arises by a different and energetically less

favoured route, although no metastable transition for their origin was found. The loss of two phenyl groups, probably in the form of biphenyl in this compound further exemplified by the formation of the ions $PhPb^+$ and $PbMn^+$ from Ph_3Pb^+ and Ph_2PbMn^+ respectively,

	m* calc.	m* found
$Ph_3Pb^+ \rightarrow PhPb^+ + Ph_2$	185.0	184.3
$Ph_2PbMn^+ \rightarrow PbMn^+ + Ph_2$	165.9	166.0

The ion $PhPb^+$ then, as in the case of the tin derivative, loses phenyl to give the lead ion.

	m* calc.	m* found
$PhPb^+ \rightarrow Pb^{+\cdot} + Ph$	151.8	152.0

The occurance of the $M\text{-}Mn^+$ ion in the tin and lead derivatives is, however, not an indication of their metal-metal bond strengths but is due to a fragmentation pattern which makes their formation easier. The loss of acetylene from benzene or the phenyl radical was also observed, as well as the loss of CO from the ion $PhCO^+$ which could be formed during the loss of Ph and CO from the molecular ion, since it is absent from the other spectra in this series.

	m* calc.	m* found
$PhCO^+ \rightarrow Ph^+ + CO$	56.5	56.4

4) <u>The $Ph_3MFe(CO)_2cp$ Derivatives</u>

The ion abundances are given in Table 4-2 and the proposed fragmentation schemes are shown in figures 4-4 to 4-7. As for the $Ph_3MMn(CO)_5$ derivatives, initial fragmentation of these compounds is by the loss of the two carbonyl groups followed by Fecp, or by the $Fe(CO)_2cp$ radical directly from the parent ion.

Table 4-1

The 70 ev Mass Spectra of the Compounds $Ph_3MMn(CO)_5$

a) Ions containing two metals:

Ion M=	Relative Abundance % Si	Ge	Sn	Pb	Ion M=	Relative Abundance % Si	Ge	Sn	Pb
$Ph_3MMn(CO)_5^+$	0.3	<0.1	0.6	0.2	$Ph_2MMn(CO)_3^+$				0.3
$Ph_3MMn(CO)_6^+$	0.1				Ph_2MMn^+				0.7
$Ph_3MMn(CO)_2^+$	0.3				$PhMMn^{++}$			0.1	0.4
Ph_3MMn^+	2.2	2.9	10.6	0.4	$C_6H_4MMn^+$			0.1	
$Ph_2MMn(CO)_5^+$				0.2	$M\text{-}Mn^+$			0.5	1.3
$Ph_2MMn(CO)_4^+$				0.3					

b) Ions containing one metal:

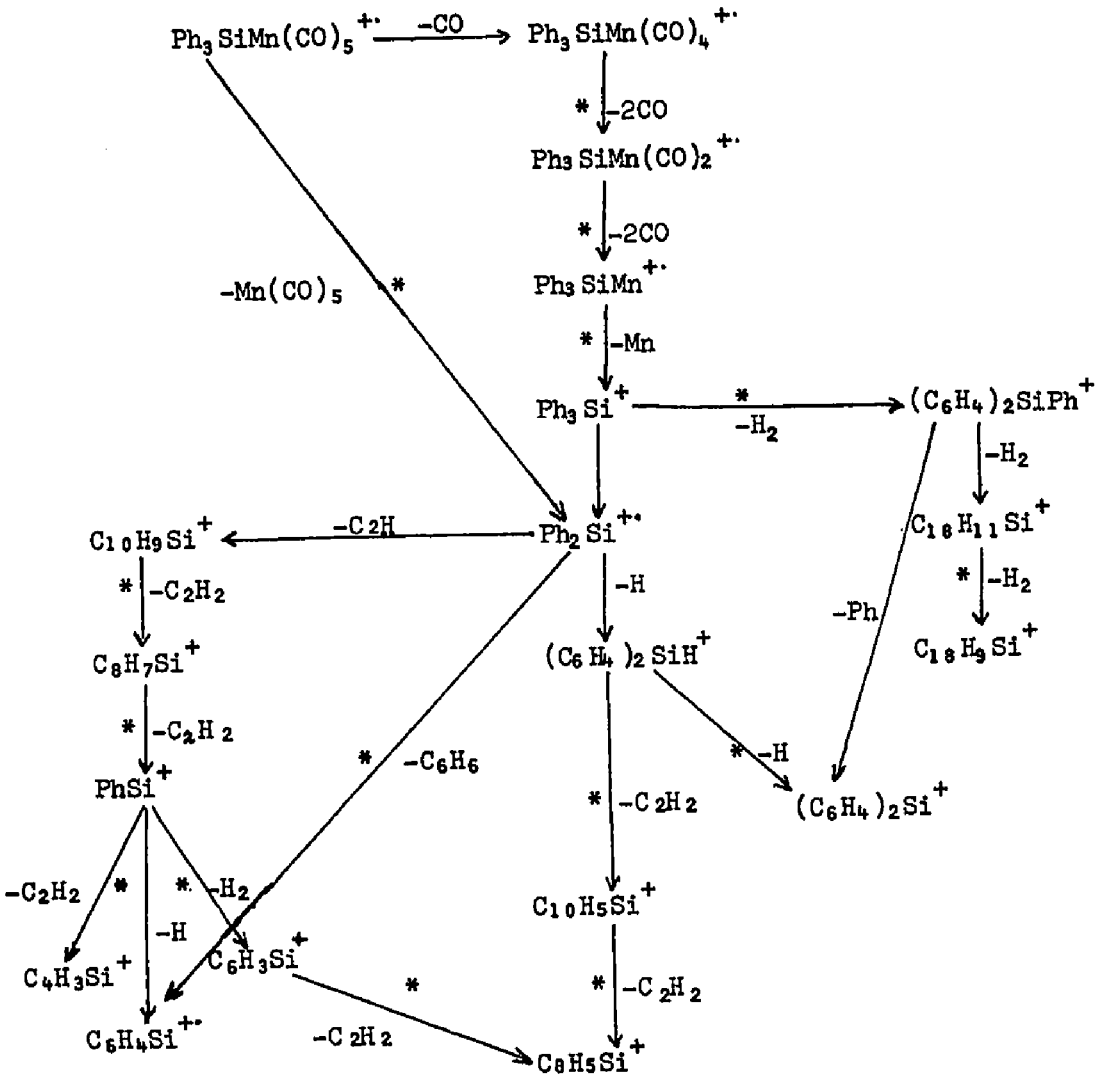
Ph_3M^+	56.2	58.9	32.4	21.7	$Mn(CO)_5^+$	0.3	0.3	[a]	0.4
$C_{18}H_{13}M^+$	1.0				$Mn(CO)_4^+$	0.3	0.3	0.2	0.3
$C_{18}H_{11}M^+$	0.7				$Mn(CO)_3^+$	0.4	0.3	0.4	0.3
$C_{18}H_9M^+$	0.5				$Mn(CO)_2^+$	0.6	0.5	0.4	0.6
$Ph_2M^{+\cdot}$	0.5	1.9	0.4		$MnCO^+$	1.1	0.9	0.7	1.2
$C_{12}H_9M^+$	5.4	2.8	0.9		$MnH^{+\cdot}$	0.3	0.2	0.1	0.3
$C_{12}H_8M^{+\cdot}$	2.0	0.9	0.2		$Ph_3Mn^{+\cdot}$				7.3
$C_{12}H_7M^+$	1.3	0.5			$PhMn^{+\cdot}$	0.4	1.6	1.3	13.7
$C_{10}H_7M^+$	1.6				Mn^+	5.0	6.9	5.5	8.6
$C_8H_7M^+$	0.3				$M^{+\cdot}$		0.2	5.4	10.1
$C_8H_5M^+$	0.9	0.2							
PhM^+	4.7	10.8	24.4	7.8					
$C_6H_4M^{+\cdot}$	0.3								
$C_6H_3M^+$	0.3								
$C_6H_2M^{+\cdot}$	0.8								

a) overlapped with $PhSn^{118+}$

Table 4-1 cont'd.

Ion M=	Relative Abundance % Si	Ge	Sn	Pb	Ion M=	Relative Abundance % Si	Ge	Sn	Pb
$C_4H_3M^+$	1.1	1.5	0.5						
C_2HM^+	1.3	1.4							
c) Hydrocarbon ions:									
$Ph_2^{+\cdot}$	0.3	0.4	0.6	1.3	$C_6H_6^{+\cdot}$	0.9	0.6	4.3	4.7
$C_{12}H_9^+$	0.4	0.2	0.3	0.4	Ph^+	0.6	0.5	0.9	1.8
$C_{12}H_8^{+\cdot}$	0.5	0.5	0.4	0.7	$C_4H_3^+$	0.4	0.6	1.1	1.7
$PhCO^+$				1.5					

Partial Fragmentation Pattern for $Ph_3SiMn(CO)_5$



* metastable transition observed

Figure 4-1

Partial Fragmentation Pattern for $Ph_3MMn(CO)_5$ (M = Ge or Sn)

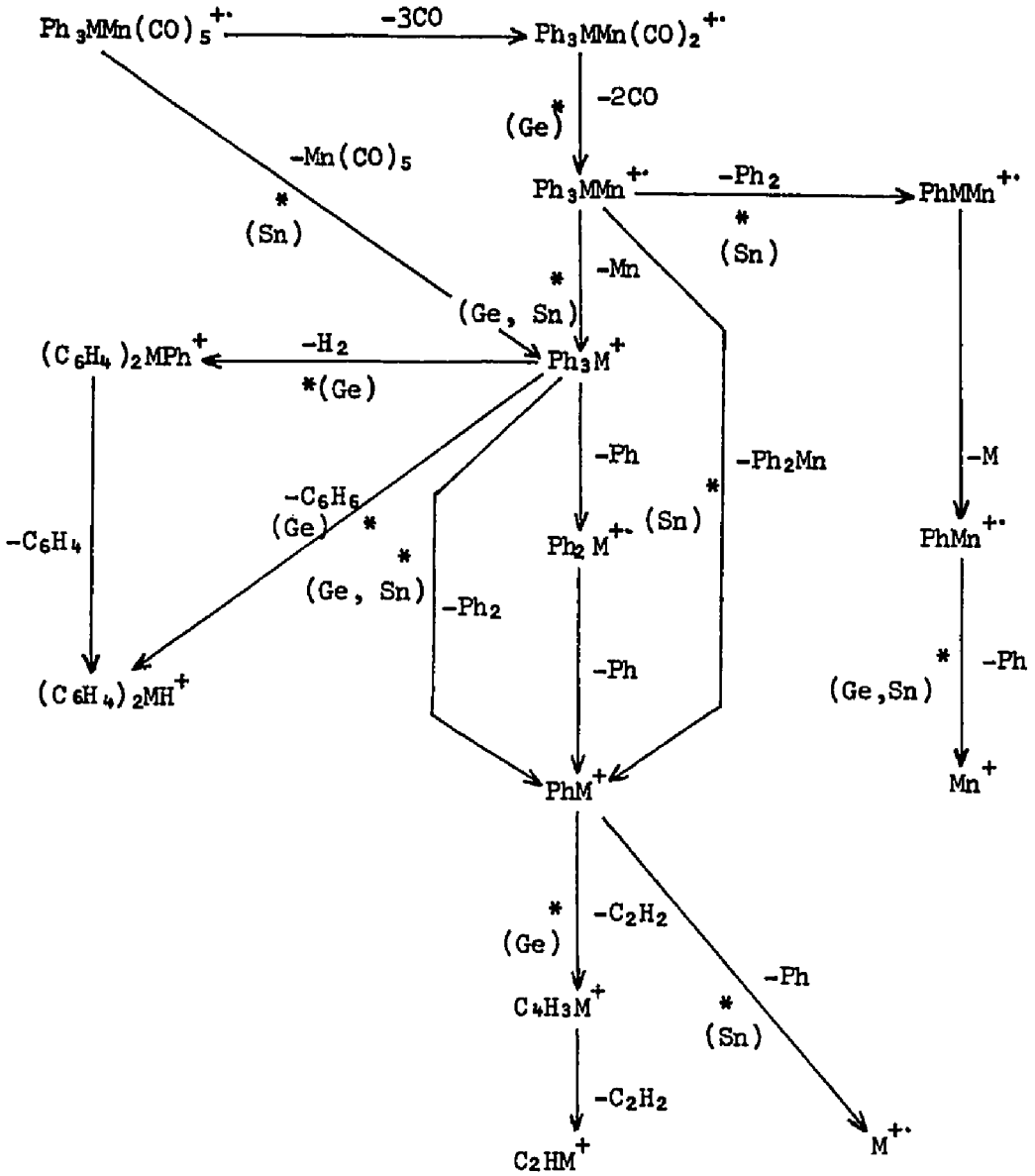


Figure 4-2

Partial Fragmentation Pattern for $Ph_3PbMn(CO)_5$

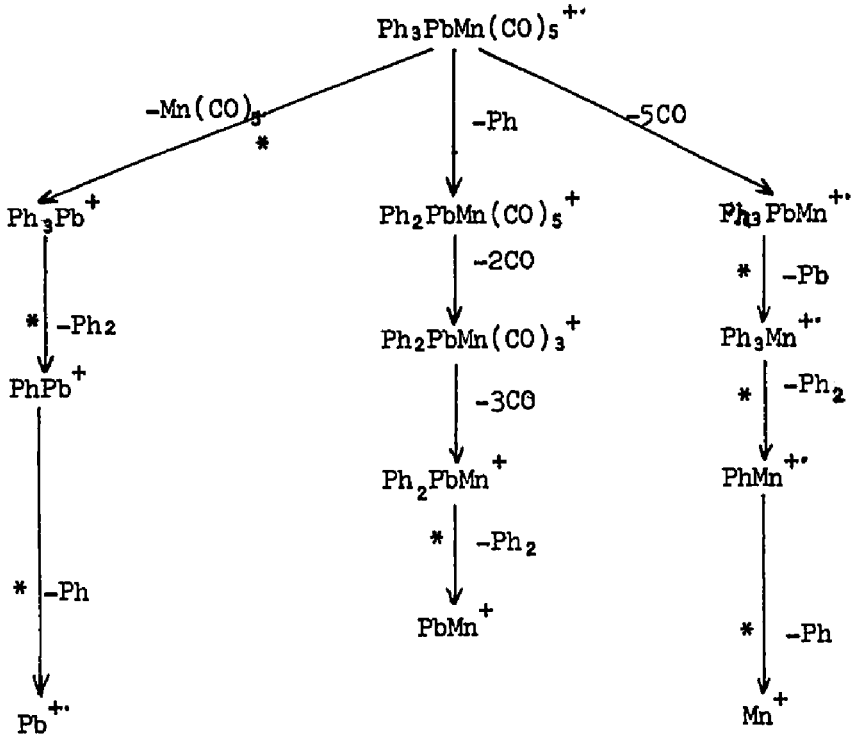


Figure 4-3

		* calc.	* found
$Ph_3MFe(CO)_2cp^{+\cdot} \rightarrow Ph_3MFe(CO)cp^{+\cdot} + CO$	M = Si	381.7	382.0
	M = Ge	427.1	427.0
	M = Sn	473.5	474.0
	M = Pb	561.4	561.5
$Ph_3MFe(CO)cp^{+\cdot} \rightarrow Ph_3MFecp^{+\cdot} + CO$	M = Si	353.9	354.0
	M = Ge	399.7	400
	M = Sn	445.6	446
$Ph_3MFecp^{+\cdot} \rightarrow Ph_3M^{+} + Fecp$	M = Ge	218.4	218.4
$Ph_3MFe(CO)_2cp^{+\cdot} \rightarrow Ph_3M^{+} + Fe(CO)_2cp$	M = Si	153.9	154.0
	M = Ge	193.0	193.0
	M = Sn	233.2	233.4
	M = Pb	312.8	313.0

For the silicon derivative, the simultaneous loss of two carbonyls from the molecular ion as well as the loss of Fe(CO)cp from the $Ph_3SiFe(CO)cp^{+\cdot}$ ion were also observed.

	* calc.	* found
$Ph_3SiFe(CO)_2cp^{+\cdot} \rightarrow Ph_3SiFecp^{+\cdot} + 2CO$	331.2	331.0
$Ph_3SiFe(CO)cp^{+\cdot} \rightarrow Ph_3Si^{+} + Fe(CO)cp$	164.8	164.8

Unlike the analogous ions formed in the spectra of the other triphenyl derivatives, the $Ph_3SiFecp^{+\cdot}$ ion shows fairly extensive loss of hydrogen or hydrogen radicals and although conclusive proof is lacking, it is likely that it is coming from the phenyl rings and not from the cyclopentadienyl ring, since there is little evidence that the $Fecp^{+}$ ion fragments in this way, and its abundance is only slightly less in this spectra than in those of the other members of the series.

Unlike $Ph_3SiMn(CO)_5$ there are more ions that still retain the silicon-iron bond, but other than those which arise by the loss of CO, the abundances of these ions are very low. The major ions in the spectra arise from the fragmentation of the base peak ion Ph_3Si^+ and follow the same pathways as those described for $Ph_3SiMn(CO)_5$. The ion formed by the loss of a hydrogen radical from $Ph_3SiFecp$ appears to control the abundances of the silicon-iron fragments, and this loses benzene to give the ion $(C_6H_4)_2SiFecp^+$.

	* calc.	* found
$Ph_3SiFecp^{+\cdot} \xrightarrow{-H} Ph_2(C_6H_4)SiFecp^+$		
$\rightarrow (C_6H_4)_2SiFecp^+ + C_6H_6$	239.1	239.0

The daughter ion then loses the Fecp radical to give $(C_6H_4)_2Si^{+\cdot}$,

	* calc.	* found
$(C_6H_4)_2SiFecp^+ \rightarrow (C_6H_4)_2Si^{+\cdot} + Fecp$	107.6	107.4

or loses cp and then Fe.

	* calc.	* found
$(C_6H_4)_2SiFe^+ \rightarrow (C_6H_4)_2Si^+ + Fe$	137.3	137.0

Alternatively, this ion could be formed by the loss of benzene from $Ph_2(C_6H_4)SiFe^+$,

	* calc.	* found
$Ph_2(C_6H_4)SiFe^+ \rightarrow (C_6H_4)_2SiFe^+ + C_6H_6$	177.4	177.5

It is difficult to rationalise the appearance of these latter ions since all the chemical reactions that involve the cleavage of the metal-metal bond occur much more readily for M-Fe bonds than do those for M-Mn bonds. However, it must be emphasised that the nature and abundances of the ions observed in a mass

spectrometer cannot be used to support conclusions about specific bond strengths, and cannot be related to the chemical reactivity of a compound especially in this case where differences in the metal-metal bond strengths are probably quite small.

The germanium compound, as well as showing the expected loss of carbonyls followed by Fecp and of $Fe(CO)_2cp$ directly, also showed the formation of $Ph_2GeFecp^+$ by loss of phenyl from $Ph_3GeFecp^{+\cdot}$

	m* calc.	m* found
$Ph_3GeFecp^{+\cdot} \rightarrow Ph_2GeFecp^+ + Ph$	286.0	286.0

This type of ion is possibly a reflection of the decrease in the Group IV metal-carbon bond strength since the $Ph_2SnFecp^+$ ion is more evident in the spectra of the tin compound, but is absent in the spectrum of the lead compound since its precursor ion $Ph_3PbFecp^+$ is also absent. As for $Ph_3GeMn(CO)_5$, the Ph_3Ge^+ ion forms the base peak and fragments by loss of benzene or biphenyl. The $PhGe^+$ ion resulting from the latter process then successively loses two molecules of acetylene to give the ions $C_4H_3Ge^+$ and C_2HGe^+. Ions containing a metal-metal bond tend to appear in slightly greater abundance than for the silicon derivative but as in this case arise by the loss of benzene and a cyclopentadienyl radical, or just benzene, from the ions $Ph_3GeFecp^+$ and $Ph_2GeFecp^+$ respectively

	m* calc.	m* found
$Ph_3GeFe \rightarrow Ph(C_6H_4)GeFe^+ + C_6H_6 + cp$	99.6	99.7
$Ph_2GeFecp^+ \rightarrow (C_6H_4)GeFecp^+ + C_6H_6$	210.4	210.4

There is also a greater tendency for the phenyl group to migrate to the iron atom and to form the ions Ph_2Fecp^+ and $PhFe(CO)_ncp^+$

(n = 0 to 2). As for the manganese pentacarbonyl derivatives these rearrangement ions become more common as the Group IV atom becomes heavier. This spectrum was also the first to show the breakdown of the Fecp ion, which occurs by two routes. The first is by loss of acetylene and the second by cleavage of the metal-ring bond.

	m* calc.	m* found
$Fecp^+ \rightarrow Fe^{+\cdot} + cp$	25.9	25.9
$Fecp^+ \rightarrow C_3H_3Fe^+ + C_2H_2$	74.6	74.5

The mass spectrum of $Ph_3SnFe(CO)_2cp$ has been previously reported (31, 172), but although the nature of the ions are the same, their intensitites greatly vary from those found in this work, and a detailed examination of the fragmentation pattern was not attempted. As for the analogous $Mn(CO)_5$ derivative this spectra shows more multiple fragmentations and a greater abudance of ions formed by rearrangements. Thus the ion $Ph_3SnFecp^{+\cdot}$ can lose a phenyl and cyclopentadienyl radical simultaneously to give Ph_2SnFe^+ or as in the case of the germanium derivative, just phenyl to give $Ph_2SnFecp^+$

	m* calc.	m* found
$Ph_3SnFecp^{+\cdot} \rightarrow Ph_2SnFecp^+ + Ph$	330.2	330.5
$Ph_3SnFecp^{+\cdot} \rightarrow Ph_2SnFe^{+\cdot} + Ph + cp$	230.7	231.0

Further fragmentation of these ions is by loss of benzene and biphenyl from the ion $Ph_2SnFe^{+\cdot}$ to give $C_6H_4SnFe^+$ and $SnFe^+$ respectively,

	m* calc.	m* found
$Ph_2SnFe^+ \rightarrow C_6H_4SnFe^+ + C_6H_6$	192.4	192.5
$Ph_2SnFe^+ \rightarrow SnFe^+ + Ph_2$	93.9	94.0

while the $cpSn^+$ ion appears to be formed by the loss of biphenyl and iron from $Ph_2SnFecp^+$.

	m* calc.	m* found
$Ph_2SnFecp^+ \rightarrow cpSn^+ + Ph_2 + Fe$	86.5	86.6

It seems very probable that the other cpM^+ ions are formed by an exactly analogous process since the relative abundances of these ions follow the same general trend as their parent fragment ions. The major fragmentation route of the Ph_3Sn^+ ion is again by the loss of biphenyl and then phenyl to give the tin ion, but the formation of Ph_2Sn^+ from Ph_3Sn^+ was also observed.

	m* calc.	m* found
$Ph_3Sn^+ \rightarrow Ph_2Sn^+ + Ph$	213.9	214.0

The breakdown of the $PhSn^+$ ion is mainly by loss of phenyl, but although the successive loss of acetylene is not a predominant feature, the ion C_2HSn^+ formed by the loss of two molecules of acetylene from PhSn was observed to give the tin ion.

	m* calc.	m* found
$C_2HSn^+ \rightarrow Sn^+ + C_2H$	99.3	99.3

The rearrangement ions also showed that the loss of phenyl or biphenyl was a fairly common process,

	m* calc.	m* found
$Ph_2Fecp^+ \rightarrow Ph_2^+ + Fecp$	86.2	86.1

but although the formation of the ion $PhFecp^+$ was not observed, the ion $C_4H_3Fecp^+$ presumably formed by the loss of acetylene from it was observed to give Fecp by cleavage of the carbon (or ring) iron bond.

	m* calc.	m* found
$C_4H_3Fecp^+ \rightarrow Fecp^+ + C_4H_3$	85.1	84.9

This is in direct contrast to the fragmentation of the $PhMn^+$ ion which was only observed to fragment only by simple cleavage of the carbon manganese bond.

In the case of the lead derivative, the abundances of the rearrangement ions and of the ions derived from these by loss of hydrogen or a hydrogen radical are greater still. The $Ph_3PbFecp^{+\cdot}$ ion is absent from the spectrum, and the abundances of the rearrangement ions appear to be controlled by the fragmentation of the ion $Ph_2PbFe(CO)_2cp^+$. This ion can fragment in two ways to give either $PhPbFecp^+$ by the loss of two carbonyls and a phenyl radical, or by loss of phenyl and lead to give $PhFe(CO)_2cp^+$.

	m* calc.	m* found
$Ph_2PbFe(CO)_2cp^+ \rightarrow PhPbFecp^{+\cdot} + Ph + 2CO$	305.8	306.0
$Ph_2PbFe(CO)_2cp^+ \rightarrow PhFe(CO)_2cp^{+\cdot} + Ph + Pb$	119.7	120.0

This latter ion, after losing its two carbonyl groups then fragments further by loss of iron or a hydrogen radical.

	m* calc.	m* found
$PhFe(CO)_2cp^{+\cdot} \xrightarrow{-2CO} PhFecp^{+\cdot} \rightarrow Phcp^{+\cdot} + Fe$	101.8	102.0
$PhFecp^{+\cdot} \rightarrow C_6H_4Fecp^+ + H$	196.0	196.0

The rearrangement ion Ph_2Fecp^+ was also observed to fragment by two routes, the first to give the ion $Fecp^+$ and biphenyl, and the second by the loss of benzene to give the ion $C_6H_4Fecp^+$.

	m* calc.	m* found
$Ph_2Fecp^+ \rightarrow Fecp^+ + Ph_2$	53.2	53.2
$Ph_2Fecp^+ \rightarrow C_6H_4Fecp^+ + C_6H_6$	141.1	141.0

Simple cleavage of the phenyliron bond was also seen to occur in the fragmentation of $PhFe(CO)cp^+$ but this metastable peak could be also due to loss of a carbonyl group from $Fe(CO)cp^+$.

	m* calc.	m* found
$PhFe(CO)cp^+ \rightarrow Fe(CO)cp^+ + Ph$	98.2	98.3
$Fe(CO)cp^+ \rightarrow Fecp^+ + CO$	98.3	98.3

The fragmentation of the ion $PhPbFecp^+$ is rather interesting since while the formation of lead and PhFecp are the only observed products both of these can form the daughter ion.

	m* calc.	m* found
$PhPbFecp^{+\cdot} \rightarrow Pb^{+\cdot} + PhFecp$	106.6	106.5
$PhPbFecp^{+\cdot} \rightarrow PhFecp^{+\cdot} + Pb$	96.6	96.8

By contrast, however, the ion $Ph_2PbFecp^+$ was observed to undergo only one transition to give the ion Ph_2Fe^+, lead and the cyclopentadienyl group, although the formation of the $cpPb^+$ ion is probably by the analogous route as that described for the formation of $cpSn^+$.

	m* calc.	m* found
$Ph_2PbFecp^+ \rightarrow Ph_2Fe^{+\cdot} + Pb + cp$	105.7	105.6

The Ph_3Pb^+ ion undergoes the usual transitions for this ion by the loss of biphenyl and then phenyl to give the lead ion which is also formed by the loss of biphenyl from the ion $Ph_2Pb^{+\cdot}$.

	m* calc.	m* found
$Ph_2Pb^{+\cdot} \rightarrow Pb^{+\cdot} + Ph_2$	119.5	119.5

5) The $(C_6F_5)_3MMn(CO)_5$ Derivatives

The ion abundances for this series are given in Table 4-3 and the proposed fragmentation schemes are shown in Figures 4-8 - 10. The molecular ions in these spectra are stronger than those for the $Ph_3MMn(CO)_5$ derivatives. In addition many more metastable transitions are seen resulting from the loss of one to four carbonyls at once, even though not all the ions resulting from such processes had a measurable abundance.

	m* calc.	m* found
$(C_6F_5)_3SiMn(CO)_5^{+\cdot} \rightarrow (C_6F_5)_3SiMn(CO)_4^{+\cdot} + CO$	669.0	669.0
$(C_6F_5)_3SiMn(CO)_5^{+\cdot} \rightarrow (C_6F_5)_3SiMn(CO)_3^{+\cdot} + 2CO$	616.3	616.0
$(C_6F_5)_3SiMn(CO)_4^{+\cdot} \rightarrow (C_6F_5)_3SiMn(CO)_2^{+\cdot} + 2CO$	589.5	589.0
$(C_6F_5)_3SiMn(CO)^{+\cdot} \rightarrow (C_6F_5)_3SiMn^{+\cdot} + CO$	557.3	558.0
$(C_6F_5)_3GeMn(CO)_5^{+\cdot} \rightarrow (C_6F_5)_3GeMn(CO)_4^{+\cdot} + CO$	715.0	715.0
$(C_6F_5)_3GeMn(CO)_4^{+\cdot} \rightarrow (C_6F_5)_3GeMn(CO)_2^{+\cdot} + 2CO$	634.2	634.0
$(C_6F_5)_3GeMn(CO)_4^{+\cdot} \rightarrow (C_6F_5)_3GeMn(CO)^{+\cdot} + 3CO$	583.5	583.5
$(C_6F_5)_3GeMn(CO)_5^{+\cdot} \rightarrow (C_6F_5)_3GeMn(CO)^{+\cdot} + 4CO$	562.3	562.0
$(C_6F_5)_3GeMn(CO)_4^{+\cdot} \rightarrow (C_6F_5)_3GeMn(CO)_3^{+\cdot} + CO$	687.1	687.0
$(C_6F_5)_3SnMn(CO)_5^{+\cdot} \rightarrow (C_6F_5)_3SnMn(CO)_4^{+\cdot} + CO$	760.9	761.0

Table 4-2

The 70 ev Mass Spectra of the Compounds $Ph_3MFe(CO)_2cp$

a) Ions containing two metals:

Ion M =	Relative Abundance % Si	Ge	Sn	Pb	Ion M =	Relative Abundance % Si	Ge	Sn	Pb
$Ph_2MFe(CO)_2cp^{+\cdot}$	2.1	1.6	2.4	0.4	$C_{17}H_{14}MFe^{+\cdot}$	0.2	0.5	2.3	
$Ph_3MFe(CO)cp^{+\cdot}$	1.3	1.8	3.8	0.1	$C_{17}H_{13}MFe^{+}$	0.4	0.5	0.3	
$Ph_3MFecp^{+\cdot}$	8.9	7.5	2.9		$C_{17}H_{12}MFe^{+\cdot}$	1.1			
$C_{23}H_{19}MFe^{+}$	4.3				$Ph_2MFe^{+\cdot}$		0.2	1.1	
$C_{23}H_{18}MFe^{+\cdot}$	2.3				$C_{12}H_8MFe^{+\cdot}$	1.2	1.0		
$C_{23}H_{17}MFe^{+}$	1.9				$PhMFecp^{+}$		0.2	1.0	0.5
$C_{23}H_{16}MFe^{+\cdot}$	1.9				$C_{11}H_8MFe^{+\cdot}$		1.7		
$Ph_2MFe(CO)_2cp^{+}$				1.2	$C_6H_4MFe^{+\cdot}$	0.3	1.9	1.9	
Ph_2MFecp^{+}	0.1	1.6	3.7	0.3	$MFe^{+\cdot}$		1.1	1.8	1.5
$C_{18}H_{14}MFe^{+\cdot}$	0.7								

b) Ions containing one metal:

Ph_3M^{+}	32.4	35.9	29.9	20.1	$M^{+\cdot}$			4.7	15.4
$C_{18}H_{13}M^{+}$	1.2				Ph_2Fecp^{+}		0.4	1.5	2.2
$C_{18}H_{11}M^{+}$	0.5				$Ph_2Fe^{+\cdot}$				1.5
$Ph_2M^{+\cdot}$	1.2	1.4	0.7	0.4	$PhFe(CO)_2cp^{+\cdot}$				1.9
$C_{12}H_9M^{+}$	4.1	2.7	0.6		$PhFe(CO)cp^{+\cdot}$				0.6
$C_{12}H_8M^{+\cdot}$	2.8	1.2	0.3		$PhFecp^{+\cdot}$	0.1	0.2	0.8	3.1
$C_{12}H_7M^{+}$	1.0	0.5			$C_{11}H_9Fe^{+}$				0.1
$C_{11}H_9M^{+}$	0.4	3.8	1.8	0.2	$C_{11}H_8Fe^{+\cdot}$		0.3	0.4	0.7
$C_{10}H_7M^{+}$	1.1				$PhFe^{+}$	0.4	0.3	0.3	0.9
$C_8H_5M^{+}$	0.7				$Fe(CO)_2cp^{+}$	0.3	0.4	0.5	0.3
PhM^{+}	3.6	9.2	7.8	11.6	$Fe(CO)cp^{+}$	0.4	0.3	0.4	0.4

Table 4-2 cont'd.

Ion M =	Relative Abundance % Si	Ge	Sn	Pb	Ion M =	Relative Abundance % Si	Ge	Sn	Pb
$Mcp^{+\cdot}$	0.6	3.7	6.9	1.2	$Fecp^{+}$	2.8	3.7	3.7	4.2
$C_4H_3M^{+}$	0.6	0.6	0.5	0.2	$C_3H_3Fe^{+}$	0.5	0.7	0.4	0.4
C_2HM^{+}	1.0	1.0	0.5	0.2	$Fe^{+\cdot}$	2.2	2.4	1.9	2.7
c) Hydrocarbon ions:									
$Ph_2^{+\cdot}$	0.3	0.3	0.5	5.8	$C_6H_6^{+\cdot}$	0.7	0.8	1.9	1.4
$C_{12}H_9^{+}$	0.3	0.2	0.2	1.2	Ph^{+}	0.4	0.6	0.6	1.7
$C_{12}H_8^{+\cdot}$	0.2	0.4	0.4	2.1	$C_4H_3^{+}$	0.3	0.2	0.7	2.9
$Phcp^{+\cdot}$	0.4	0.4	0.6	0.7					
$C_{11}H_9^{+}$		0.4	0.6	0.7					

Partial Fragmentation Pattern for $Ph_3SiFe(CO)_2cp$

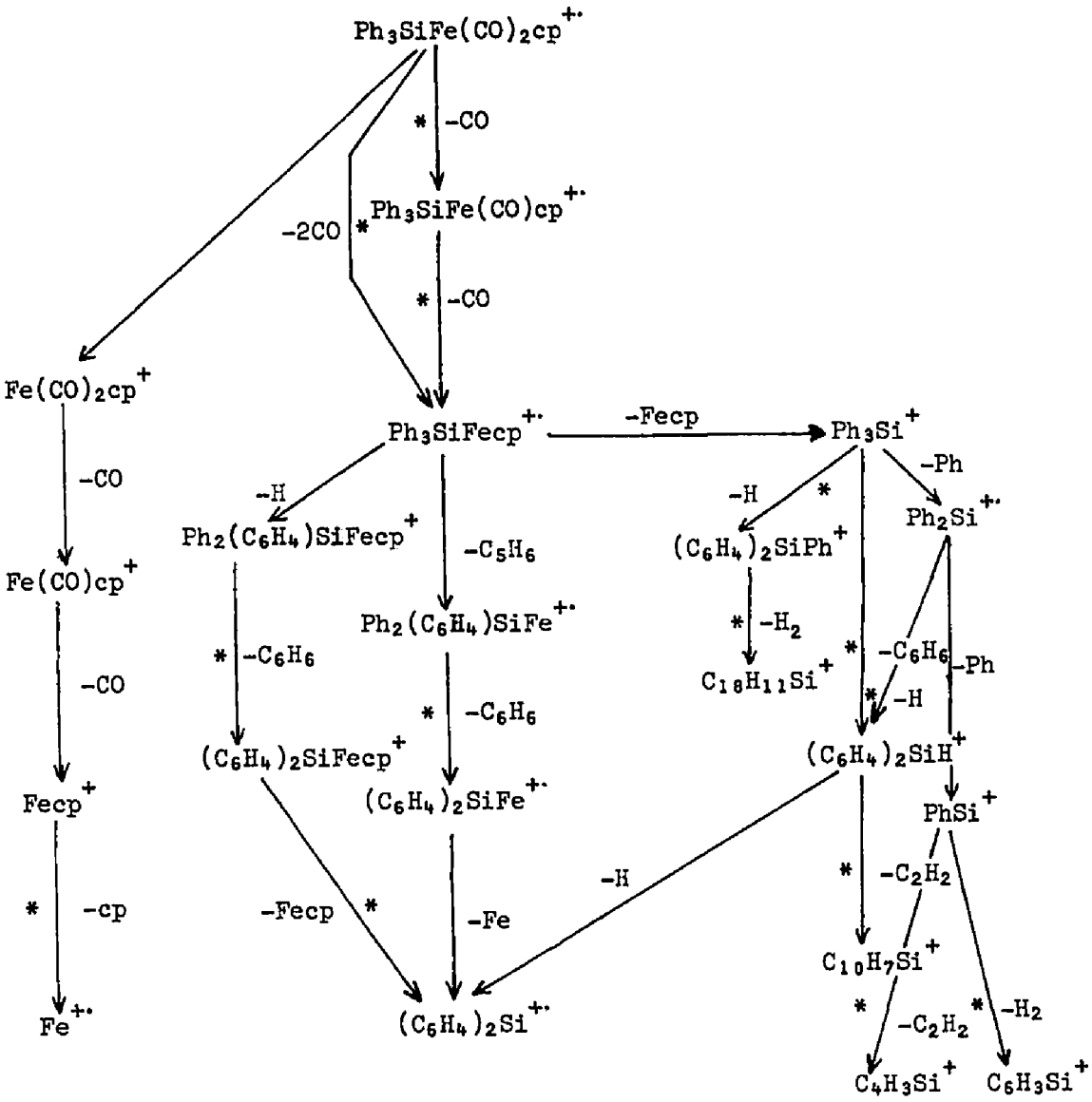


Figure 4-4

Partial Fragmentation Pattern for $Ph_3GeFe(CO)_2cp$

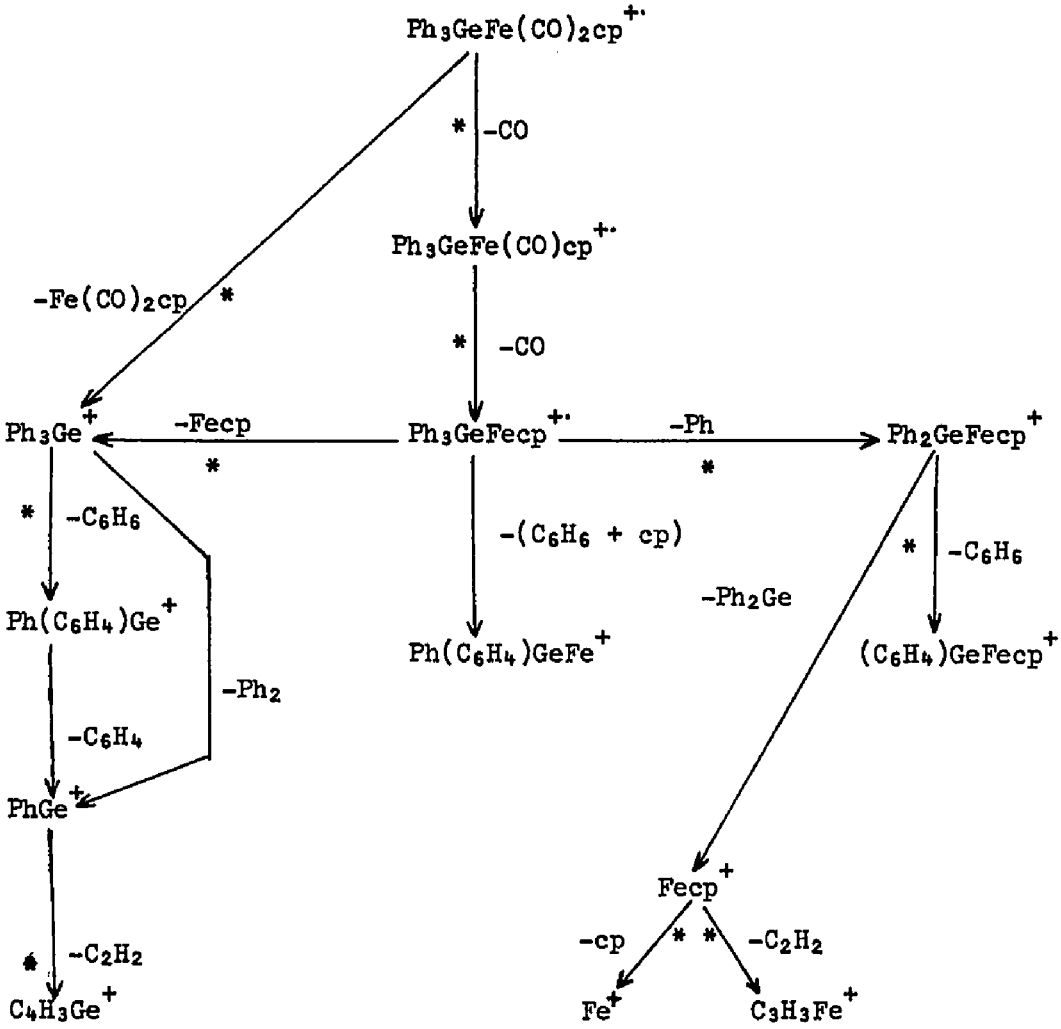


Figure 4-5

Partial Fragmentation Pattern for $Ph_3SnFe(CO)_2cp$

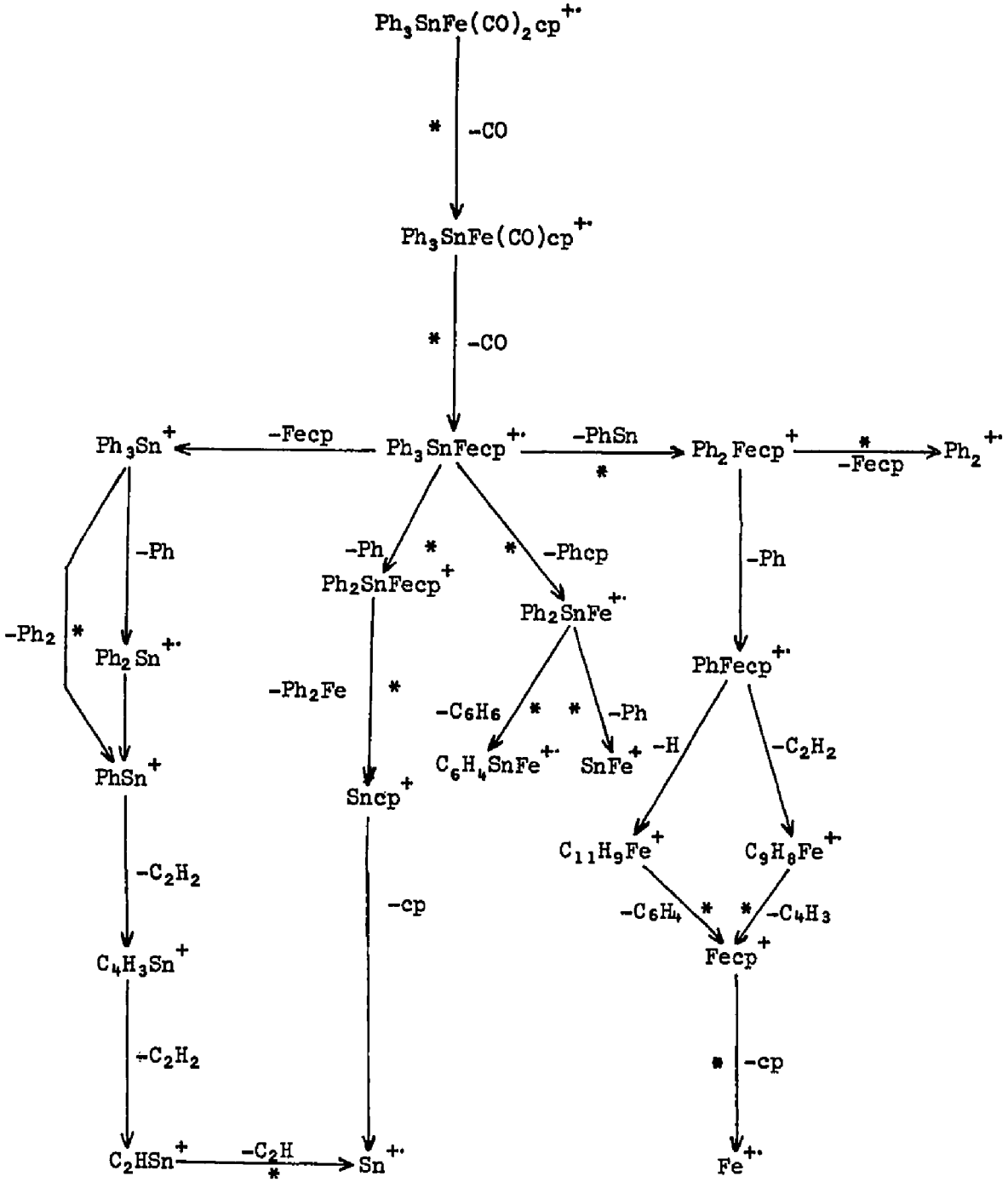


Figure 4-6

Partial Fragmentation Pattern for $Ph_3PbFe(CO)_2cp$

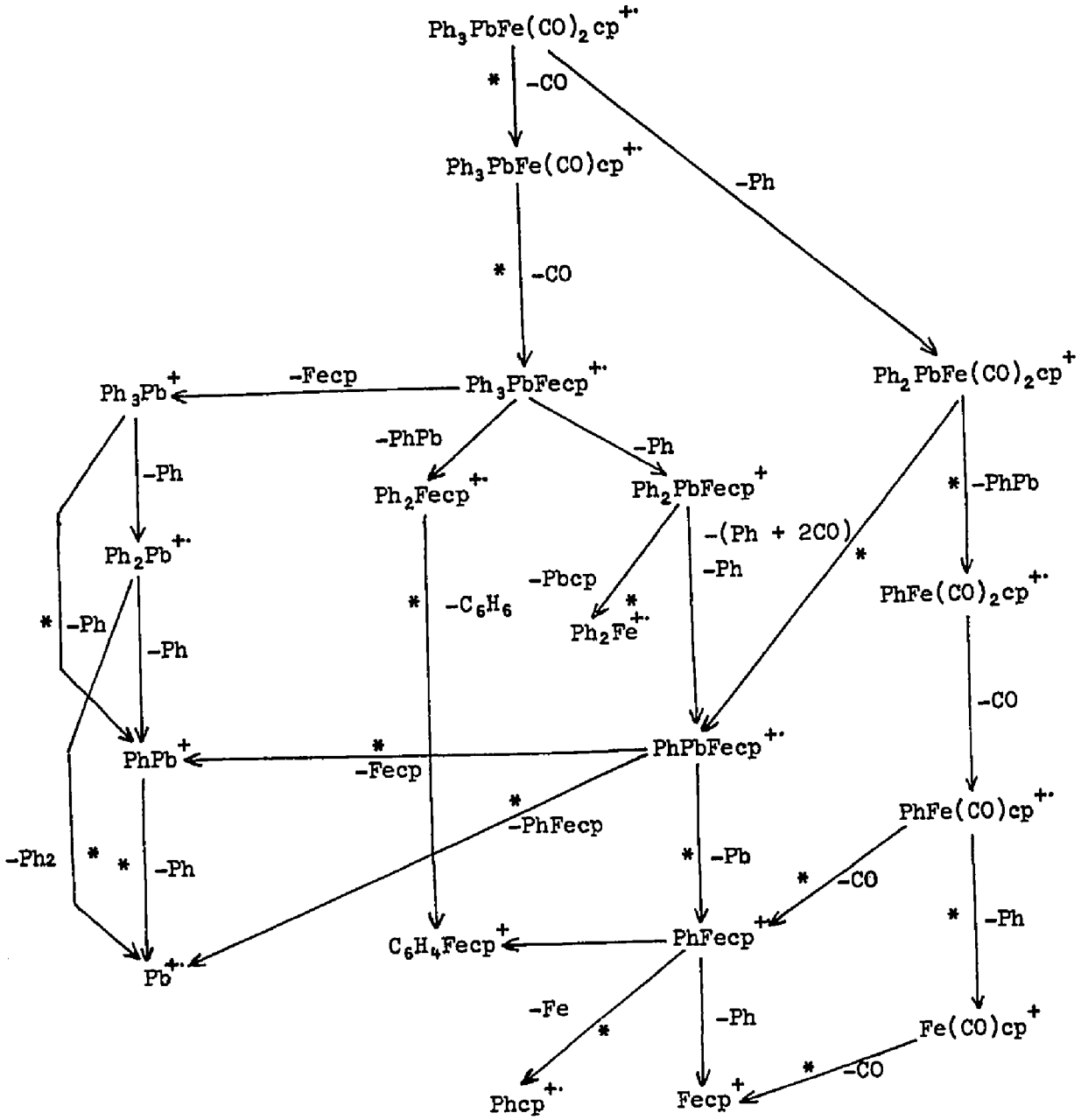


Figure 4-7

	m* calc.	m* found
$(C_6F_5)_3SnMn(CO)_4^{+\cdot} \rightarrow (C_6F_5)_3SnMn(CO)^{+\cdot} + 3CO$	628.7	629.0
$(C_6F_5)_3SnMn(CO)_4^{+\cdot} \rightarrow (C_6F_5)_3SnMn^{+\cdot} + 4CO$	607.3	607.0
$(C_6F_5)_3SnMn(CO)_5^{+\cdot} \rightarrow (C_6F_5)_3SnMnCO^{+\cdot} + 4CO$	579.9	580.0

By contrast, only the silicon derivative showed the loss of $Mn(CO)_5$ directly,

	m* calc.	m* found
$(C_6F_5)_3SiMn(CO)_5^{+\cdot} \rightarrow (C_6F_5)_3Si^{+} + Mn(CO)_5$	385.5	386.0

while the loss of manganese from the ion $(C_6F_5)_3MMn^+$ was not observed in any of the spectra.

This suggests that for these compounds, the main fragmentation mode is not by loss of manganese from the $(C_6F_5)_3MMn^+$ ion, but by the loss of manganese and metal fluoride species. Comparison of the relative abundances for the ions $(C_6F_5)_3MMn^+$ and $(C_6F_5)M^+$ tends to support this conclusion since the abundances of the latter are quite small, but are not known to be particularly unstable since the mass spectra of the tetrakis(pentafluorophenyl) derivatives of Group IV all show large abundances of the $(C_6F_5)_3M^+$ ion(181). The fact that the ions $C_6F_5^+$ and $Mn(CO)_4^+$ have the same nominal mass to charge ratio caused problems in the identification of some of the ions. Thus, $(C_6F_5)_2MMn(CO)_5^+$ and $(C_6F_5)_2MMn(CO)_4^+$ can be alternatively formulated as $(C_6F_5)_3MCO^+$ and $(C_6F_5)_3M^+$ respectively but since the spectra of $(C_6F_5)_3MFe(CO)_2cp$ (M = Ge or Sn) show peaks that can only be due to the loss of C_6F_5, an analogous process has been assumed to take place in this case and is further supported by the observance of the metastable peaks for the transitions

	m* calc.	m* found
$(C_6F_5)_3SiMn(CO)_2^{+\cdot} \rightarrow (C_6F_5)_2SiMn(CO)_2^{+} + C_6F_5$	349.6	350.0
$(C_6F_5)_3SiMn(CO)_3^{+\cdot} \rightarrow (C_6F_5)_2SiMn(CO)_2^{+} C_6F_5CO$	334.9	335.0

The $(C_6F_5)_3M^+$ ion should be present in all spectra at least to some degree and is formulated as such, although the germanium derivative did show the transition

	m* calc.	m* found
$(C_6F_5)_2GeMn(CO)_5^{+} \rightarrow (C_6F_5)_2GeMn(CO)_4^{+} + CO$	548.3	548.0

There is probably some contribution to the $(C_6F_5)_3M^+$ ion from ions of this type but this cannot be very great since none of the ions resulting from a loss of carbonyl or the normally fairly intense metastable peaks associated with these transitions were observed.

However, the tin spectrum did show the transition

	m* calc.	m* found
$C_6F_5SnCO^{+} \rightarrow C_6F_5Sn^{+} + CO$	261.5	261.0

and this is assumed to be correct since the alternative formulation of this ion as $SnMn(CO)_5^{+}$ is rather unlikely, and no ions or metastable transitions for its fragmentation by the loss of CO were observed.

This ion is not as novel as might be expected since the products obtained from the cocondensation of tin and germanium vapours with CO at very low temperatures have been claimed on the basis of their infrared spectra, to be the binary carbonyls $M(CO)_2$ (M= Ge or Sn) (199). However, since the origin of the species C_6F_5SnCO was not found, this could equally well be formed by a gas phase reaction between C_6F_5Sn radical ions and CO, and not as a result of the ionisation and fragmentation of the parent compound.

The mass spectrum of the silicon compound is extremely complex, making the assignment of many of the ions uncertain or impossible and resulting in a rather low total percentage abundance. No attempt will be made to describe all the metastable transitions particularly those involving just the fluorocarbon ions, but the fragmentation of this compound is controlled by the very intense ion $(C_6F_5)_3SiMn^{+\cdot}$ and to a lesser extent by $(C_6F_5)_3Si^+$. There are three main routes, the first of these being the loss of a silicon and manganese fluoride species to give a fluorocarbon ion.

	m* calc.	m* found
$(C_6F_5)_3SiMn^{+\cdot} \rightarrow (C_6F_4)_3^{+\cdot} + F_3SiMn$	337.5	337.0
$(C_6F_5)_3SiMn^{+\cdot} \rightarrow C_{18}F_{10}^{+\cdot} + F_3SiMnF_2$	281.5	282.0
$(C_6F_5)_3SiMn^{+\cdot} \rightarrow C_{12}F_7^+ + C_6F_5(F)_2SiMnF$	131.5	131.3

The formation of these ions is not indescriminant since there is a noticable lack of ions containing between 13 and 16, 7 and 11 and 2 and 4 carbon atoms. Fragmentation between two ions that contain the same number of carbon atoms is nearly always by loss of a fluoride radical,

	m* calc.	m* found
$C_{18}F_{11}^+ \rightarrow C_{18}F_{10}^{+\cdot} + F$	387.8	388.0
$C_{18}F_8^{+\cdot} \rightarrow C_{18}F_7^+ + F$	331.0	331.0
$C_{17}F_9^+ \rightarrow C_{17}F_9^{+\cdot} + F$	337.5	337.5

while those between two ions that differ by only one carbon atom are almost exclusively by the loss of CF_2.

	m* calc.	m* found
$C_{18}F_{11}^+ \rightarrow C_{17}F_9^+ + CF_2$	330.9	331.0

	m* calc.	m* found
$C_{18}F_9^+ \rightarrow C_{17}F_9^+ + CF_2$	293.5	293.5
$C_{12}F_7^+ \rightarrow C_{11}F_5^+ + CF_2$	149.5	149.5
$C_6F_5^+ \rightarrow C_5F^+ + CF_2$	48.4	48.6

Fragmentation of a fluorocarbon by loss of a radical species containing five or six carbon atoms however appears to depend on the stability of the parent and daughter ion and no particular species appears to be favoured.

	m* calc.	m* found
$C_{18}F_9^+ \rightarrow C_{12}F_6^{+\cdot} + C_6F_3$	171.8	172.0
$C_{18}F_8^{+\cdot} \rightarrow C_{12}F_4^{+\cdot} + C_6F_4$	131.5	131.5
$C_{17}F_7^+ \rightarrow C_{12}F_4^{+\cdot} + C_5F_3$	143.6	144.0
$C_{17}F_9^+ \rightarrow C_{12}F_8^+ + C_5F$	143.6	144.0

The second route is the fragmentation of a silicon-fluorocarbon ion by loss of a silicon fluoride species,

	m* calc.	m* found
$C_{18}F_{13}Si^+ \rightarrow C_{18}F_9^+ + SiF_4$	305.0	305.0
$C_{11}F_7Si^+ \rightarrow C_{11}F_3^+ + SiF_4$	121.9	122.0
$C_{11}F_9Si^+ \rightarrow C_{11}F_8^{+\cdot} + SiF$	243.7	244.0
$C_{17}F_9Si^+ \rightarrow C_{17}F_7^+ + SiF_2$	281.8	281.5
$C_{17}F_{11}Si^+ \rightarrow C_{17}F_9^+ + SiF_2$	318.9	319.0
$(C_6F_5)_3Si^+ \rightarrow (C_6F_4)_2^{+\cdot} + C_6F_5SiF_2$	165.5	166.0
$C_{17}F_{11}Si^+ \rightarrow C_{17}F_8^{+\cdot} + SiF_3$	287.4	287.0

although a loss of a fluorine or fluorocarbon radical, especially C_6F_4, is often observed and this latter process tends to become more dominant for the heavier derivatives of Group IV.

	m* calc.	m* found
$C_{12}F_9Si^+ \rightarrow C_{11}F_7Si^+ + CF_2$	250.3	250.5
$(C_6F_5)_2Si^{+\cdot} \rightarrow C_{12}F_9Si^+ + F$	325.0	325.0
$C_{17}F_{11}Si^+ \rightarrow C_{11}F_7Si^+ + C_6F_4$	250.3	250.5
$(C_6F_5)_3Si^+ \rightarrow C_{17}F_{13}Si^+ + CF_2$	433.7	434.0
$(C_6F_5)_3Si^+ \rightarrow C_6F_5SiF_2^+ + (C_6F_4)_2$	102.5	102.5
$(C_6F_5)_3Si^+ \rightarrow C_{12}F_{13}Si^+ + C_6F_2$	331.9	332.0

A similar process also occurs for the $C_6F_5Mn^{+\cdot}$ ion,

	m* calc.	m* found
$C_6F_5Mn^{+\cdot} \rightarrow MnF^{+\cdot} + C_6F_4$	24.7	24.7

The third route is by the loss of a manganese fluoride species

	m* calc.	m* found
$(C_6F_5)_3SiMn^{+\cdot} \rightarrow C_{18}F_{13}Si^+ + MnF_2$	412.8	413.0
$(C_6F_5)_3SiMn^{+\cdot} \rightarrow C_{18}F_{12}Si^+ + MnF_3$	381.5	381.5
$(C_6F_5)_3SiMn^{+\cdot} \rightarrow C_{12}F_9Si^+ + C_6F_5MnF$	201.5	202.0
$(C_6F_5)_2Si(F)Mn^{+\cdot} \rightarrow C_{12}F_9Si^+ + MnF_2$	269.8	270.0
$(C_6F_5)_2Si(F)Mn^{+\cdot} \rightarrow C_{12}F_8Si^{+\cdot} + MnF_3$	240.5	240.7

and the loss of C_6F_4 from the ion $(C_6F_5)_3SiMn$ is also observed.

	m* calc.	m* found
$(C_6F_5)_3SiMn^{+\cdot} \rightarrow (C_6F_5)_2Si(F)Mn^{+\cdot} + C_6F_4$	325.5	325.5

For the germanium derivative, although there is some loss of germanium and manganese fluorides from the ions $(C_6F_5)_3GeMn^{+\cdot}$ $(C_6F_5)_3Ge^+$, $(C_6F_5)_2Ge(F)Mn^{+\cdot}$ and $(C_6F_5)_2GeF^+$,

	m* calc.	m* found
$(C_6F_5)_3GeMn^{+\cdot} \rightarrow (C_6F_4)_3^{+\cdot} + F_3GeMn$	312.9	313.0

	m* calc.	m* found
$(C_6F_5)_3Ge^+ \rightarrow (C_6F_4)_3^{+\cdot} + GeF_3$	342.8	343.0
$(C_6F_5)_2Ge(F)Mn^{+\cdot} \rightarrow C_{12}F_6^{+\cdot} + F_3GeMnF_2$	138.1	138.0
$(C_6F_5)_2GeF^+ \rightarrow (C_6F_4)_2^{+\cdot} + GeF_3$	205.2	205.0
$C_6F_5Ge^+ \rightarrow C_6F_4^+ + GeF$	90.9	91.0

the high abundance of the ion $C_6F_5Ge^+$, and the observation of the metastable peak describing the transition,

	m* calc.	m* found
$(C_6F_5)_3GeMn^+ \rightarrow C_6F_5Ge^+ + (C_6F_5)_2Mn$	92.2	92.0

shows that this route is dominating the fragmentation. Unlike the silicon derivative, there is little tendency for this compound to fragment by loss of MF_4 or MF_2 species, and the major fragmentation mode is by the loss of C_6F_4 and C_6F_5 radicals neither of which were found to be very common for the silicon derivative,

	m* calc.	m* found
$(C_6F_5)_3GeMn^{+\cdot} \rightarrow (C_6F_5)_2Ge(F)Mn^{+\cdot} + C_6F_4$	368.7	369.0
$(C_6F_5)_3Ge^+ \rightarrow (C_6F_5)_2GeF^+ + C_6F_4$	317.1	317.0
$(C_6F_5)_2Ge(F)Mn^{+\cdot} \rightarrow C_6F_5Ge(F)Mn^+ + C_6F_5$	205.9	206.0
$C_6F_5Ge^+ \rightarrow GeF^+ + C_6F_4$	35.9	35.9

and the loss of $(C_6F_5)_2Ge$ was also observed.

	m* calc.	m* found
$(C_6F_5)_3Ge^+ \rightarrow C_6F_5^+ + (C_6F_5)_2Ge$	48.5	48.5

The ion $(C_6F_5)_3GeF$ is probably formed as a result of an ion-molecule reaction and not as a result of an impurity or the thermal pyrolysis of the sample in the inlet system. The most obvious impurity is $(C_6F_5)_4Ge$, but it is rather difficult to see how this

could be formed during the preparation of the compound $(C_6F_5)_3GeMn(CO)_5$. Moreover, the mass spectrum of $(C_6F_5)_4Ge$ (181) shows only a small abundance of $(C_6F_5)_3GeF^{+\cdot}$ and the very much more abundant ion $(C_6F_5)_4Ge^{+\cdot}$ was not observed in the present case. This was the only manganese pentacarbonyl derivative to show ions of this type even though they were also observed in the series $(C_6F_5)_3MFe(CO)_2cp$. The mass spectrum of the compound $Ph(C_6F_5)_2SiMn(CO)_5$ also showed the ions $Ph(C_6F_5)_2SiF^{+\cdot}$ and $(C_6F_5)_2SiF^{+}$, but the analogous tin and germanium ions were not observed in the mass spectra of these derivatives. Since the silicon derivatives are probably more stable, these effects are probably not a result of thermal pyrolysis. The mass spectrum of $Ph_2(C_6F_5)SnFe(CO)_2cp$ also showed the ion Ph_3Sn^{+}, which if it was due to the compound $Ph_3SnFe(CO)_2cp$ would represent a 10% impurity in the sample of $Ph_2(C_6F_5)SnFe(CO)_2cp$ and would thus be revealed by a low fluorine analysis. Since the analysis was within 0.2% of the calculated values it would appear that this ion was also formed by an ion-molecule reaction.

For the tin derivative, the fragmentation is even more simplified, there being only a few fluorocarbon ions present such that nearly all the ion current is carried by the metal containing ions. As for the germanium derivative the dominant fragmentation mode is by loss of $(C_6F_5)_2Mn$ from the ion $(C_6F_5)_3SnMn^{+\cdot}$,

	m* calc.	m* found
$(C_6F_5)_3SnMn^{+\cdot} \rightarrow C_6F_5Sn^{+} + (C_6F_5)_2Mn$	121.9	122.0

Similarly, the loss of C_6F_4 is also observed and appears to be the exclusive process for the formation of the ions $(C_6F_5)_2SnF^{+}$, and SnF^{+},

	m* calc.	m* found
$(C_6F_5)_3Sn^+ \rightarrow (C_6F_5)_2SnF^+ + C_6F_4$	360.3	360.0
$C_6F_5Sn^+ \rightarrow SnF^+ + C_6F_4$	67.3	67.3

and is similar to that observed in the mass spectra of the series $(C_6F_5)_4M$ (181). The correlation of the abundances of the MF^+ ions to the abundances of the $C_6F_5M^+$ ions suggest that the formation of these fluorides is by the loss of C_6F_4, but although the analogous transition for the production of MnF from $C_6F_5Mn^+$ was observed for the silicon and germanium derivatives, the large abundance of the MnF^+ ion formed from a relatively weak C_6F_5Mn ion in the mass spectra of the silicon derivative suggests that at least in this case, some other process might be responsible.

Various ions of the series $Mn(CO)_n^+$ (n = 0 to 5) were also seen and these fragment by the successive loss of a carbonyl group even though all the appropriate metastable peaks were not observed. The transition

	m* calc.	m* found
$Mn(CO)_4^+ \rightarrow Mn(CO)_3^+ + CO$	115.7	115.7

was however observed in nearly all cases and appears to be particularly favoured.

Although none of the compounds contain hydrogen there are ions present that can only be reasonably assigned to $C_6F_5H^+$ and $C_5F_2H^+$. Similar ions have been noticed in the mass spectra of the compounds $(C_6F_5)_3M$ (M = Group V) and probably arise by the abstraction of a hydrogen radical from the background water vapour or hydrocarbon fragments by the good scavenger C_6F_6 (185).

Table 4-3

The 70 ev. Mass Spectra of the Compounds $(C_6F_5)_3MMn(CO)_5$

a) Ions containing two metals:

Ion M =	Relative Abundance % Si	Ge	Sn
$(C_6F_5)_3MMn(CO)_5^{+\cdot}$	0.9	2.2	5.7
$(C_6F_5)_3MMn(CO)_4^{+\cdot}$	3.5	1.5	0.5
$(C_6F_5)_3MMn(CO)_2^{+\cdot}$	0.7		
$(C_6F_5)_3MMnCO^{+\cdot}$	2.0	1.9	0.9
$(C_6F_5)_3MMn^{+\cdot}$	16.2	11.1	5.1
$C_{15}F_{13}MMn(CO)_2^{+\cdot}$	0.3		
$C_{15}F_{12}MMn(CO)_2^{+\cdot}$	0.5		
$(C_6F_5)_2MMn(CO)_5^{+}$		0.4	0.8
$(C_6F_5)_2FMMn^{+\cdot}$		0.6	0.3
$(C_6F_5)_2MMn^{+}$			0.3
$(C_6F_5)F_2MMn^{+\cdot}$		0.7	
$F_3MMn^{+\cdot}$		2.4	3.1

b) Ions containing one metal:

$(C_6F_5)_3MF^{+\cdot}$		0.5[d]	
$(C_6F_5)_3M^{+}$ / $(C_6F_5)_2MMn(CO)_4^{+}$	0.4	3.1	3.0
$C_{18}F_{14}M^{+\cdot}$	0.2		
$C_{18}F_{13}M^{+}$	0.4		
$C_{18}F_{12}M^{+\cdot}$	1.8		
$C_{17}F_{13}M^{+}$	0.3		
$C_{17}F_{11}M^{+}$	1.3		

d) ion formed by ion molecule reaction

Table 4-3 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$(C_6F_5)_2MF^+$		0.5	0.9
$(C_6F_5)_2M^{+\cdot}$	0.5		
$C_{12}F_9M^+$	1.4	0.4	
$C_{11}F_9M^+$	0.5		
$C_{12}F_8M^+$	0.6		
$C_6F_5MCO^+$			0.9
$C_6F_5MF_2^+$	0.2	0.3	0.4
$C_6F_5M^+$	0.8	21.0	28.5
$MF_3^{+\cdot}$	0.8		
MF^+	1.1	16.5	24.2
$M^{+\cdot}$		0.3	1.8
$Mn(CO)_5^+$	a	2.9	2.6
$Mn(CO)_4^+$	0.6	2.1	1.6
$Mn(CO)_3^+$	0.6	0.8	b
$Mn(CO)_2^+$	0.6	0.5	0.6
$MnCO^+$	0.9	0.9	1.3
Mn^+	4.0	2.8	2.8
$C_6F_5Mn^{+\cdot}$	1.9	0.9	0.7
$MnF_3^{+\cdot}$	0.2		
MnF_2^+	0.2		
$MnF^{+\cdot}$	7.5	3.4	2.6
c) Fluorocarbon Ions:			
$C_{18}F_{13}^+$		0.1	

a) overlapped with $C_6F_5Si^+$
b) overlapped with $Sn^{120}F^+$

Table 4-3 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_{18}F_{12}^{+\cdot}$	0.2	0.3	0.1
$C_{18}F_{11}^{+}$	0.1	0.1	
$C_{18}F_{10}^{+\cdot}$	1.9	0.7	0.1
$C_{18}F_{9}^{+}$	0.7		
$C_{18}F_{8}^{+\cdot}$	2.5		
$C_{17}F_{11}^{+}$	0.1		
$C_{17}F_{9}^{+}$	1.1	0.4	
$C_{17}F_{8}^{+\cdot}$	0.2		
$C_{17}F_{7}^{+}$	2.0		
$C_{17}F_{6}^{+\cdot}$	0.3		
$C_{17}F_{5}^{+}$	0.3		
$C_{12}F_{9}^{+}$		0.2	
$C_{12}F_{8}^{+\cdot}$	0.6	1.7	0.4
$C_{12}F_{7}^{+}$	2.2	0.7	
$C_{12}F_{6}^{+\cdot}$	1.7		
$C_{12}F_{5}^{+}$	1.5		
$C_{12}F_{4}^{+\cdot}$	0.2		
$C_{11}F_{7}^{+}$	0.2	0.4	0.2
$C_{11}F_{6}^{+\cdot}$	0.2	0.6	
$C_{11}F_{5}^{+}$	1.4	1.0	
$C_{11}F_{4}^{+\cdot}$	0.4	0.2	
$C_{11}F_{3}^{+}$	1.9	0.4	0.2
$C_{6}F_{5}H^{+\cdot}$	0.6	0.3	1.0
$C_{6}F_{5}^{+}$ c			

c) overlapped with $Mn(CO)_4^+$

Table 4-3 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_6F_4^{+\cdot}$	0.9	1.1	0.7
$C_6F_3^{+}$	0.2	0.8	0.4
$C_6F_2^{+\cdot}$	0.7	0.5	0.5
C_6F^{+}	0.5		
$C_5F_3^{+}$	0.9	0.5	0.4
$C_5F_2H^{+}$	0.4	0.2	0.6
$C_5F_2^{+\cdot}$	0.6	0.4	0.4
C_5F^{+}	1.0	0.7	0.7

Partial Fragmentation Pattern for $(C_6F_5)_3SiMn(CO)_5$

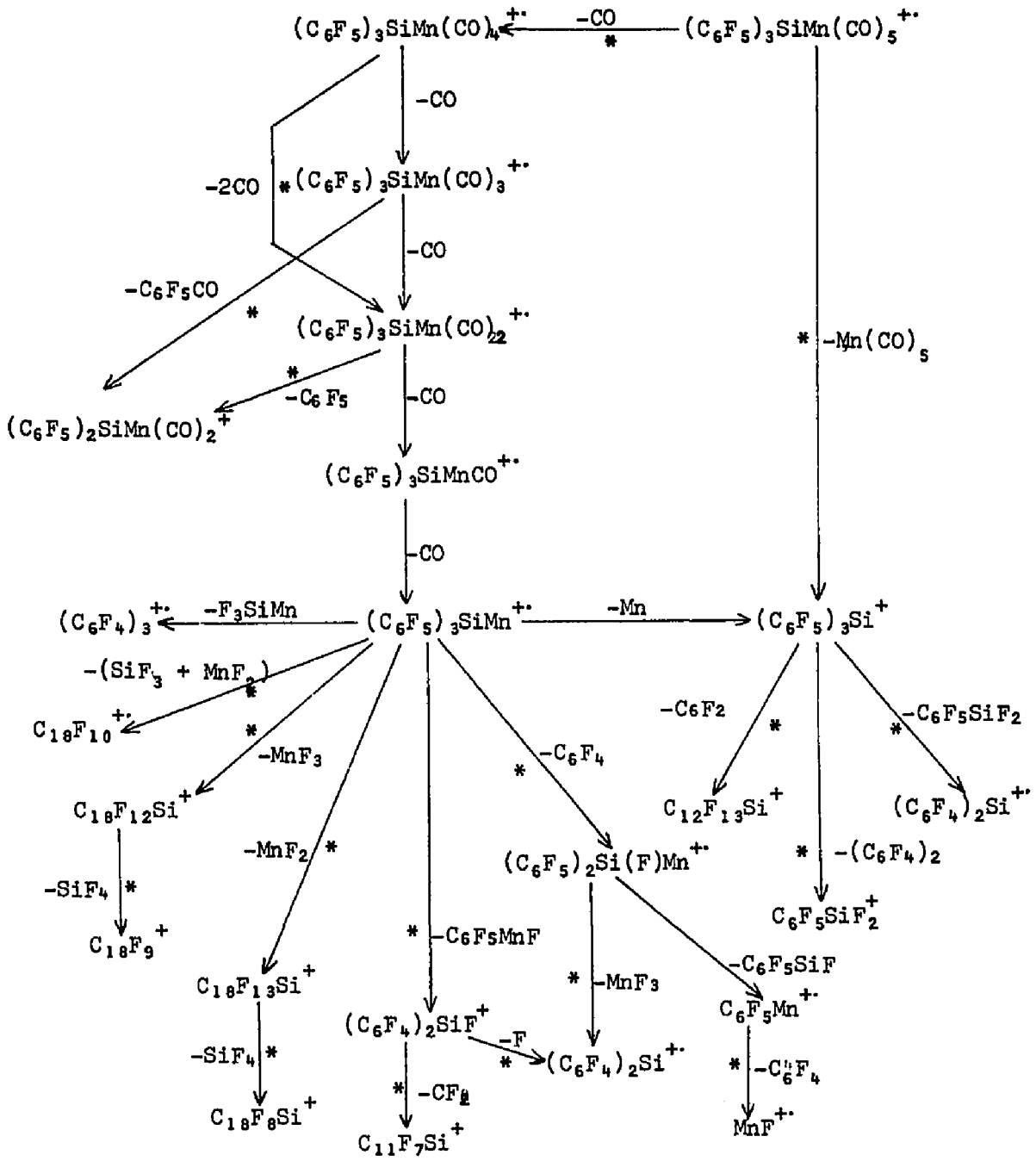


Figure 4-8

Partial Fragmentation Pattern for $(C_6F_5)_3GeMn(CO)_5$

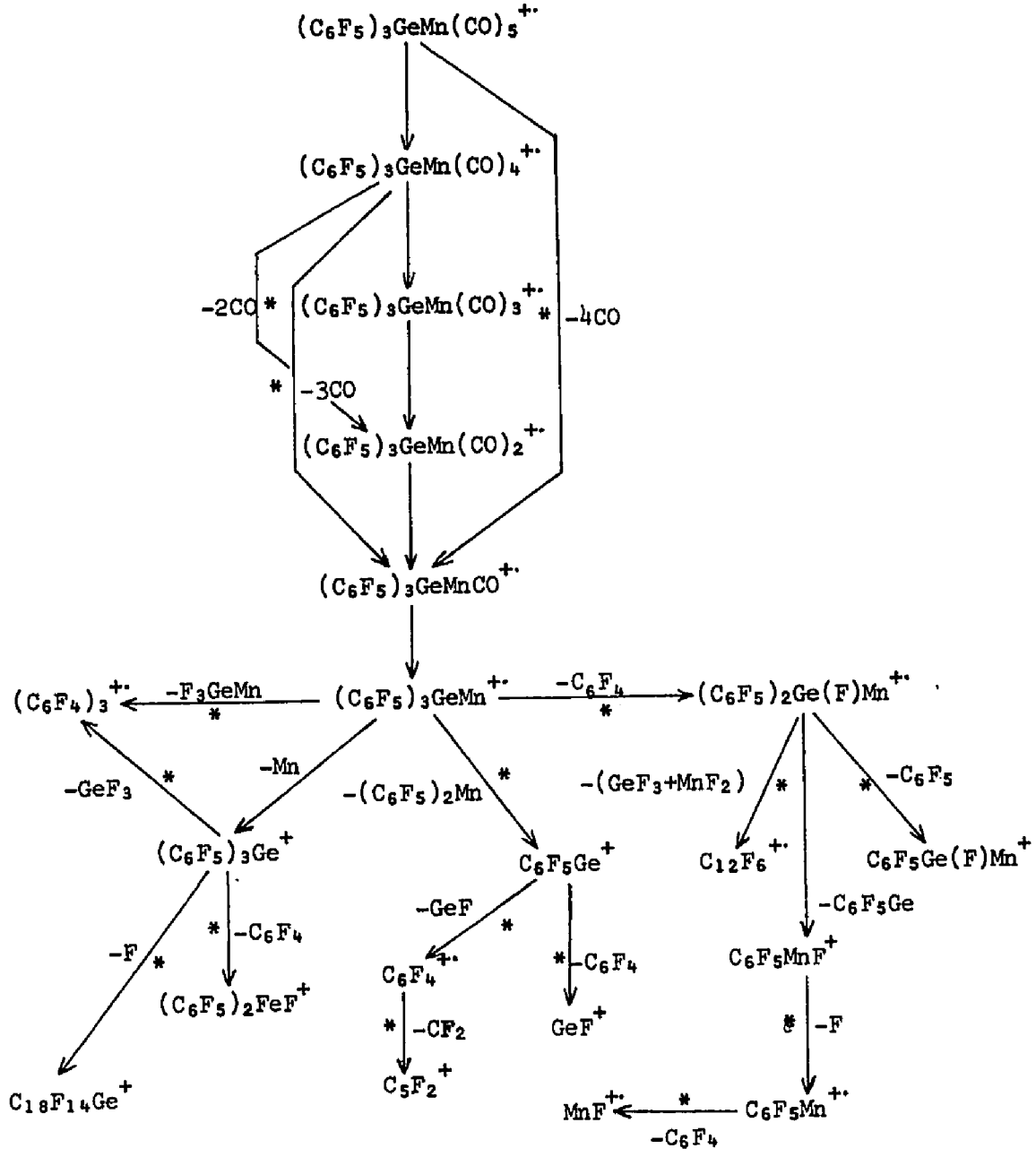


Figure 4-9

Partial Fragmentation Pattern for $(C_6F_5)_3SnMn(CO)_5$

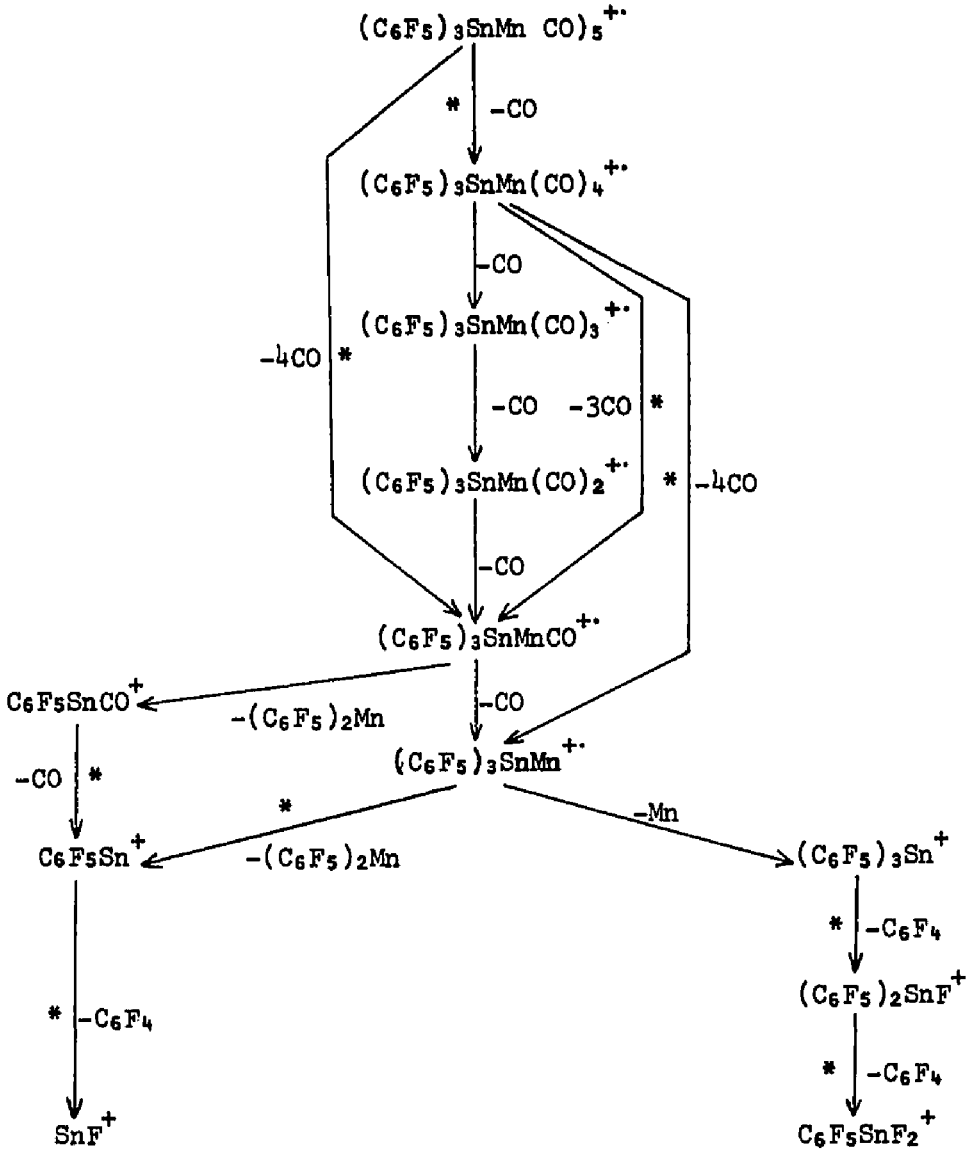


Figure 4-10

6) The $(C_6F_5)_3MFe(CO)_2cp$ Derivatives

The ion abundances for this series are given in Table 4-4 and the proposed fragmentation schemes are shown in Figures 4-11 to 4-13. The usual stepwise loss of carbonyl is observed in all these derivatives, but the loss of $Fe(CO)_2cp$ directly was not observed in any case although the silicon derivative did show the loss of $Fe(CO)cp$ from $(C_6F_5)_3SiFe(CO)cp^{+\cdot}$. The loss of $Fecp$ from the ion $(C_6F_5)_3MFecp^{+\cdot}$ was not found to be at all common, and as for the analogous derivatives of manganese pentacarbonyl these spectra showed only small abundances of the ion $(C_6F_5)_3M^+$

	m* calc.	m* found
$(C_6F_5)_3SiFe(CO)_2cp^{+\cdot} \rightarrow (C_6F_5)_3SiFe(CO)cp^{+\cdot} + CO$	649.2	649.0
$(C_6F_5)_3SiFe(CO)cp^{+\cdot} \rightarrow (C_6F_5)_3SiFecp^{+\cdot} + CO$	632.2	632.0
$(C_6F_5)_3SiFe(CO)cp^{+\cdot} \rightarrow (C_6F_5)_3Si^+ + Fe(CO)cp$	412.7	413.0
$(C_6F_5)_3GeFe(CO)_2cp^{+\cdot} \rightarrow (C_6F_5)_3GeFe(CO)cp^{+\cdot} + CO$	677.0	677.0
$(C_6F_5)_3GeFe(CO)cp^{+\cdot} \rightarrow (C_6F_5)_3GeFecp^{+\cdot} + CO$	669.1	669.0
$(C_6F_5)_3SnFe(CO)_2cp^{+\cdot} \rightarrow (C_6F_5)_3SnFe(CO)cp^{+\cdot} + CO$	743.6	744.0
$(C_6F_5)_3SnFe(CO)cp^{+\cdot} \rightarrow (C_6F_5)_3SnFe(cp)^{+\cdot} + CO$	715.0	715.0

Very small abundances of the ions due to the loss of a C_6F_5 radical from the parent ion were apparent for the germanium and tin derivatives but only the germanium derivative showed the transition,

	m* calc.	m* found
$(C_6F_5)_3GeFe(CO)_2cp^{+\cdot} \rightarrow (C_6F_5)_2GeFe(CO)_2cp^+ + C_6F_5$	455.1	455.0

As for the manganese pentacarbonyl derivatives, the main fragmentation takes place from the ion $(C_6F_5)_3GeFecp^{+\cdot}$ and not from the relatively unabundant $(C_6F_5)_3M^+$ ions.

The fragmentation of the silicon derivative is again very complex

and only two thirds of the peaks measured could be adequately assigned. The main mode of fragmentation of the ion $(C_6F_5)_3SiFecp^{+\cdot}$ is by the loss of a metal fluoride species,

	m* calc.	m* found
$(C_6F_5)_3SiFecp^{+\cdot} \rightarrow (C_6F_4)_3^{+\cdot} + F_3SiFecp$	303.3	303.0
$(C_6F_5)_3SiFecp^{+\cdot} \rightarrow C_{18}F_{12}Sicp^{+} + FeF_3$	433.7	434.0
$(C_6F_5)_3SiFecp^{+\cdot} \rightarrow C_{18}F_{13}Sicp^{+\cdot} + FeF_2$	475.5	475.6

while the base peak $FFecp^{+}$ appears to arise mainly by the loss of a fluorocarbon species $C_{18}F_{14}Si$,

	m* calc.	m* found
$(C_6F_5)_3SiFecp^{+\cdot} \rightarrow FFecp^{+\cdot} + C_{18}F_{14}Si$	30.2	30.2

and the loss of a fluorine radical is also observed.

	m* calc.	m* found
$(C_6F_5)_3SiFecp^{+\cdot} \rightarrow C_{18}F_{14}SiFecp^{+} + F$	612.5	613.0

The ion $C_{18}F_{14}SiFecp^{+}$ then fragments further by loss of Fecp or C_6F_5Fecp to give the ions $C_{18}F_{14}Si^{+}$ and $C_{12}F_9Si^{+}$ respectively.

	m* calc.	m* found
$C_{18}F_{14}SiFecp^{+} \rightarrow C_{18}F_{14}Si^{+\cdot} + Fecp$	412.2	412.0
$C_{18}F_{14}SiFecp^{+} \rightarrow C_{12}F_9Si^{+} + C_6F_5Fecp$	186.4	186.0

Loss of a silicon fluoride species is the main mode of fragmentation for the ions containing only silicon,

	m* calc.	m* found
$C_{18}F_{12}Sicp^{+} \rightarrow C_{18}F_{10}cp^{+} + SiF_2$	413.1	413.0
$C_{18}F_{13}Sicp^{+\cdot} \rightarrow C_{12}F_7^{+} + C_6F_5Si(F)cp$	138.0	138.0
$C_{12}F_9Si^{+\cdot} \rightarrow C_{12}F_7^{+} + SiF$	236.8	237.0

although the loss of a fluorocarbon species is still important,

	m* calc.	m* found
$(C_6F_5)_3Si^+ \rightarrow (C_6F_5)_2Si^{+\cdot} + C_6F_5$	247.5	248.0
$(C_6F_5)_2Si^{+\cdot} \rightarrow C_{11}F_7Si^+ + CF_3$	237.2	237.0
$C_6F_5Si^+ \rightarrow C_5F_4Si^{+\cdot} + CF$	137.9	138.0
$C_{17}F_{11}Si^+ \rightarrow C_{11}F_9Si^+ + C_6F_2$	284.2	284.0
$C_{18}F_{14}Si^{+\cdot} \rightarrow (C_6F_5)_2SiF^+ + C_6F_3$	284.6	285.0
$C_{17}F_{11}Si^+ \rightarrow C_{12}F_9Si^+ + C_5F_2$	266.8	267.0
$C_{12}F_9Si^+ \rightarrow C_{11}F_8Si^{+\cdot} + CF$	283.8	284.0

and thus takes place in much the same way as fragmentation of the fluorocarbon-silicon ions derived from $(C_6F_5)_3SiMn(CO)_5$.

Unlike the other two members of this series, there is no appreciable abundance of the ion $C_6F_5Fecp^{+\cdot}$ although the ion $FFecp^{+\cdot}$ forms the base peak. This is presumably formed by the loss of $C_{18}F_{14}Si$ from the ion $(C_6F_5)_3SiFecp^{+\cdot}$ as previously described, and not by the loss of C_6F_4 which is the most dominant mode for the production of $MnF^{+\cdot}$ and MF^+ ions. The $FFecp^{+\cdot}$ ion fragments by loss of cp or HF,

	m* calc.	m* found
$FFecp^{+\cdot} \rightarrow FeF^+ + cp$	40.2	40.2
$FFecp^{+\cdot} \rightarrow FeC_5H_4^{+\cdot} + HF$	102.8	102.9

and this has also been observed in the spectrum of $C_6F_5Fe(CO)_2cp$ (200). Even though the main fragmentation route is from the ion $(C_6F_5)_3MFecp^{+\cdot}$, some cleavage of the metal-metal bond occurs since in common with the germanium and tin derivatives the characteristic stepwise loss of CO and then finally cp from the ion $Fe(CO)_2cp^+$ is always observed.

	m* calc.	m* found
$Fe(CO)_2cp^+ \rightarrow Fe(CO)cp^+ + CO$	125.4	125.5
$Fe(CO)cp^+ \rightarrow Fecp^+ + CO$	98.3	98.3
$Fecp^+ \rightarrow Fe^{+\cdot} + cp$	25.9	25.9

The mass spectrum of the germanium derivative shows the loss of a metal fluoride species to be less important, the major fragmentation pathway being the loss of $(C_6F_5)_2Ge$ from the very intense ion $(C_6F_5)_3GeFecp^{+\cdot}$

	m* calc.	m* found
$(C_6F_5)_3GeFecp^{+\cdot} \rightarrow C_6F_5Fecp^{+\cdot} + (C_6F_5)_2Ge$	119.1	119.0

This process probably accounts for the very low abundance of the $C_6F_5Ge^+$ ion compared to that observed in the spectrum of $(C_6F_5)_3GeMn(CO)_5$, where the most dominant fragmentation process leads to the formation of this ion.

The ion $C_6F_5Fecp^{+\cdot}$ then fragments by loss of HF or an iron fluoride species, to give the ions $C_6F_4cp^+$, $C_6F_3cp^{+\cdot}$, and $C_6F_4FeC_5H_4^{+\cdot}$

	m* calc.	m* found
$C_6F_5Fecp^{+\cdot} \rightarrow C_6F_4cp^+ + FeF$	157.5	157.5
$C_6F_5Fecp^{+\cdot} \rightarrow C_6F_3cp^{+\cdot} + FeF_2$	130.7	131.0
$C_6F_5Fecp^{+\cdot} \rightarrow C_6F_4FeC_5H_4^{+\cdot} + HF$	249.4	249.5

which then further lose HF or FeF_2.

	m* calc.	m* found
$C_6F_3cp^{+\cdot} \rightarrow C_6F_2C_5H_4^{+\cdot} + HF$	156.1	156.0
$C_6F_4FeC_5H_4^{+\cdot} \rightarrow C_6F_2C_5H_4^{+\cdot} + FeF_2$	113.0	113.0

These processes have also been observed for the $C_6F_5Fecp^+$ ion derived from $C_6F_5Fe(CO)_2cp$ (200).

The ion $(C_6F_5)_2GeFe(CO)_2cp^+$ formed by the loss of a C_6F_5 radical from the parent ion was observed to fragment by loss of $Fe(CO)_2cp$,

	m* calc.	m* found
$(C_6F_5)_2GeFe(CO)_2cp^+ \rightarrow (C_6F_5)_2Ge^{+\cdot} + Fe(CO)_2cp$	284.5	285.0

while the ions $(C_6F_5)_3Ge^+$ and $(C_6F_5)_2GeF^+$ were observed to lose GeF_3 rather than C_6F_4 which is more common for these heavier pentafluorophenyl derivatives of Group IV (181, 183).

	m* calc.	m* found
$(C_6F_5)_3Ge^+ \rightarrow C_{18}F_{12}^{+\cdot} + GeF_3$	205.2	205.0
$(C_6F_5)_2GeF^+ \rightarrow C_{12}F_8^{+\cdot} + GeF_3$	342.8	343.0

In common with its hydrocarbon analogue the spectrum of this compound showed some rather unusual but relatively weak ions that were almost completely absent in the spectra of the other derivatives. These were presumably formed by the loss of C_6F_5FeF from $(C_6F_5)_3GeFecp^{+\cdot}$ to give $(C_6F_5)(C_6F_4)Gecp^{+\cdot}$, which then lost a hydrogen radical and fragmented further by loss of C_6F_4 and then HF.

	m* calc.	m* found
$(C_6F_4)(C_6F_5)GeC_5H_4^+ \rightarrow C_6F_5GeC_5H_4^+ + C_6F_4$	205.4	205.0
$C_6F_5GeC_5H_4^{+\cdot} \rightarrow C_6F_4GeC_5H_3^{+\cdot} + HF$	266.3	266.0

For the tin derivative, although the formation of the ion $(C_6F_5)_3Sn^+$ becomes more important, the dominant fragmentation mode is still by loss of $(C_6F_5)_2Sn$ from $(C_6F_5)_3SnFecp^{+\cdot}$.

	m* calc.	m* found
$(C_6F_5)_3SnFecp^{+\cdot} \rightarrow C_6F_5Fecp^{+\cdot} + (C_6F_5)_2Sn$	111.8	111.5

The ion $C_6F_5Fecp^{+\cdot}$ then fragments by loss of FeF, FeF_2 and HF in a

manner exactly analogous to that described for the germanium derivative. Another, but very minor route for the fragmentation of the $(C_6F_5)_3SnFecp^{+\cdot}$ ion is by the loss of C_6F_5Sn or C_6F_5,

	m* calc.	m* found
$(C_6F_5)_3SnFecp^{+\cdot} \rightarrow (C_6F_5)_2Fecp^{+} + C_6F_5Sn$	279.0	279.0
$(C_6F_5)_3SnFecp^{+\cdot} \rightarrow (C_6F_5)_2SnFecp^{+} + C_6F_5$	445.5	445.5

Even though the ions resulting from the fragmentation of the ion $(C_6F_5)_3Sn^{+}$ by successive loss of C_6F_4 are more abundant than the analogous ions in the spectra of the germanium and silicon compounds, only the loss of the first C_6F_4 group was observed.

	m* calc.	m* found
$(C_6F_5)_3Sn^{+} \rightarrow (C_6F_5)SnF^{+} + C_6F_4$	360.2	360.0

7) The $Ph_2(C_6F_5)MMn(CO)_5$ Derivatives

The relative abundances and fragmentation patterns for these derivatives are given in Table 4-5 and the proposed fragmentation patterns are shown in Figures 4-14 to 16. These spectra bear a much greater resemblance to the $Ph_3MMn(CO)_5$ derivatives than to their fluorocarbon analogues. Ions due to the loss of carbonyl groups from the molecular ion are quite weak and in all cases the loss of the first carbonyl and of $Mn(CO)_5$ were observed. The loss of manganese from the ion $Ph_2(C_6F_5)MMn^{+\cdot}$ was observed for the silicon and germanium derivatives, and probably occurs to an equal extent in the tin derivative since the abundance of the daughter ion is higher in this derivative, while the abundances of the ion $Ph_2(C_6F_5)MMn^{+\cdot}$ remain essentially constant.

Table 4-4

The 70 e.v. Mass Spectra of the Compounds $(C_6F_5)_3MFe(CO)_2cp$

a) Ions containing two metals:

Ion M =	Relative Abundance % Si	Ge	Sn
$(C_6F_5)_3MFe(CO)_2cp^{+\cdot}$	0.5	1.3	4.0
$(C_6F_5)_3MFe(CO)cp^{+\cdot}$	5.8	4.7	1.8
$(C_6F_5)_3MFecp^{+\cdot}$	5.5	15.2	6.7
$C_{18}F_{14}MFecp^{+}$	1.3		
$(C_6F_5)_2MFe(CO)_2cp^{+}$		0.2	0.4
$(C_6F_5)_2MFecp^{+}$	0.1	0.1	0.4
$(C_6F_5)_2MFe^{+\cdot}$			0.4
$C_6F_4MFe^{+\cdot}$		1.5	

b) Ions containing one metal:

$(C_6F_5)_3MF^{+\cdot}$ a)	0.3	0.2	1.6
$(C_6F_5)_3M^{+}$	0.1	1.7	2.2
$C_{18}F_{14}Mcp^{+}$	0.1		
$C_{18}F_{13}Mcp^{+\cdot}$	0.3		
$C_{18}F_{12}Mcp^{+}$	0.2		
$C_{18}F_{13}MC_5H_4^{+}$	0.3		
$C_{18}F_{12}MC_5H_3^{+}$	0.2		
$C_{18}F_{14}M^{+\cdot}$	0.3		
$C_{18}F_{11}MC_5H_6^{+}$	0.3		
$C_{18}F_{12}M^{+\cdot}$	0.2		
$C_{17}F_{13}M^{+}$	0.2		
$C_{17}F_{11}M^{+}$	0.4		
$C_{12}F_9Mcp^{+\cdot}$	0.2	0.4	

a) Ion formed by ion-molecule reaction

Table 4-4 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_{12}F_9MC_5H_4^+$	0.3		
$(C_6F_5)_2MF^+$	0.2	0.6	1.6
$(C_6F_5)_2M^{+\cdot}$	0.7		
$C_{12}F_9M^+$	0.2		
$C_{11}F_9M^+$	0.7		
$C_6F_5MF_2^+$	0.3	0.2	0.5
$C_6F_4MC_5H_4^{+\cdot}$		1.4	0.6
$C_6F_5M^+$	0.1	1.3	6.1
cpM^+	0.7	1.0	1.3
MF^+	0.4	8.5	12.4
$M^{+\cdot}$		0.3	1.1
$(C_6F_5)_2Fecp^+$			0.1
$C_6F_5Fecp^{+\cdot}$		2.8	6.1
$C_6F_4FeC_5H_4^{+\cdot}$	0.4	5.5	5.5
$FFe(CO)cp^{+\cdot}$ b)			
$FFecp^{+\cdot}$	9.0	4.1	3.5
$Fe(CO)_2cp^+$	0.8	1.4	1.4
$Fe(CO)cp^+$	1.5	2.1	2.1
$Fecp^+$	7.8	4.9	3.5
$FeC_3H_3^+$	0.8	1.1	0.6
$FeF_2^{+\cdot}$	0.8	0.5	0.4
FeF^+	0.3	1.2	1.1
$Fe^{+\cdot}$	2.2	2.1	1.7

b) overlapped with $C_6F_5H^{+\cdot}$

Table 4-4 cont'd

c) Hydrocarbon/Fluorocarbon ions:

Ion M =	Relative Abundance % Si	Ge	Sn
$C_{18}F_{12}^{+\cdot}$	0.2		
$C_{18}F_{11}^{+}$	0.2		
$C_{18}F_{10}^{+\cdot}$	0.9		
$C_{18}F_{9}^{+}$	0.8		
$C_{18}F_{8}^{+\cdot}$	0.8		
$C_{17}F_{13}^{+}$	0.8		
$C_{17}F_{12}^{+\cdot}$	0.2		
$C_{17}F_{11}^{+}$	0.6		
$C_{17}F_{10}^{+\cdot}$	0.1		
$C_{17}F_{9}^{+}$	0.9		
$C_{17}F_{8}^{+\cdot}$	0.2		
$C_{17}F_{7}^{+}$	0.9	0.1	
$C_{17}F_{6}^{+\cdot}$	0.1		
$C_{17}F_{5}^{+}$	0.1		
$C_{12}F_{9}^{+}$		0.3	0.3
$C_{12}F_{8}^{+\cdot}$	0.7	2.9	0.5
$C_{12}F_{7}^{+}$	1.5	0.7	0.1
$C_{12}F_{6}^{+\cdot}$	1.3	1.3	0.2
$C_{12}F_{5}^{+}$	0.4		
$C_{12}F_{4}^{+\cdot}$	0.1		
$C_{11}F_{9}^{+}$	1.2		
$C_{11}F_{8}^{+\cdot}$	0.4		
$C_{11}F_{7}^{+}$	0.3	0.6	0.3

Table 4-4 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_{11}F_6^{+\cdot}$	0.2		
$C_{11}F_5^{+}$	1.4	0.6	0.2
$C_{11}F_4^{+\cdot}$	0.3		
$C_{11}F_5H_5^{+\cdot}$		0.2	0.3
$C_{11}F_4H_5^{+}$	0.3	1.3	1.2
$C_{11}F_3H_5^{+\cdot}$	0.4	3.4	3.5
$C_{11}F_3H_4^{+}$	0.8	2.7	2.6
$C_{11}F_3H_3^{+\cdot}$	0.1	0.7	0.6
$C_{11}F_2H_5^{+}$		0.9	1.4
$C_{11}F_2H_4^{+\cdot}$	0.4	1.8	1.8
$C_{10}F_8^{+\cdot}$	0.1		
$C_{10}F_7^{+}$	0.1		
$C_{10}F_6^{+\cdot}$	0.2		
$C_6F_5H^{+\cdot}$	0.8	1.1	2.4
$C_6F_5^{+}$	0.1	0.9	0.5
$C_6F_3^{+}$	1.8	0.8	0.3
$C_5F_3^{+}$	0.5	0.5	0.5
$C_5F_2H^{+}$	0.6	0.6	1.1
C_5F^{+}	0.6	0.3	0.3
cp^{+}	1.8	1.6	1.0

Table 4-4 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_{11}F_6^{+\cdot}$	0.2		
$C_{11}F_5^{+}$	1.4	0.6	0.2
$C_{11}F_4^{+\cdot}$	0.3		
$C_{11}F_5H_5^{+\cdot}$		0.2	0.3
$C_{11}F_4H_5^{+}$	0.3	1.3	1.2
$C_{11}F_3H_5^{+\cdot}$	0.4	3.4	3.5
$C_{11}F_3H_4^{+}$	0.8	2.7	2.6
$C_{11}F_3H_3^{+\cdot}$	0.1	0.7	0.6
$C_{11}F_2H_5^{+}$		0.9	1.4
$C_{11}F_2H_4^{+\cdot}$	0.4	1.8	1.8
$C_{10}F_8^{+\cdot}$	0.1		
$C_{10}F_7^{+}$	0.1		
$C_{10}F_6^{+\cdot}$	0.2		
$C_6F_5H^{+\cdot}$	0.8	1.1	2.4
$C_6F_5^{+}$	0.1	0.9	0.5
$C_6F_3^{+}$	1.8	0.8	0.3
$C_5F_3^{+}$	0.5	0.5	0.5
$C_5F_2H^{+}$	0.6	0.6	1.1
C_5F^{+}	0.6	0.3	0.3
cp^{+}	1.8	1.6	1.0

Partial Fragmentation Pattern for $(C_6F_5)_3SiFe(CO)_2cp$

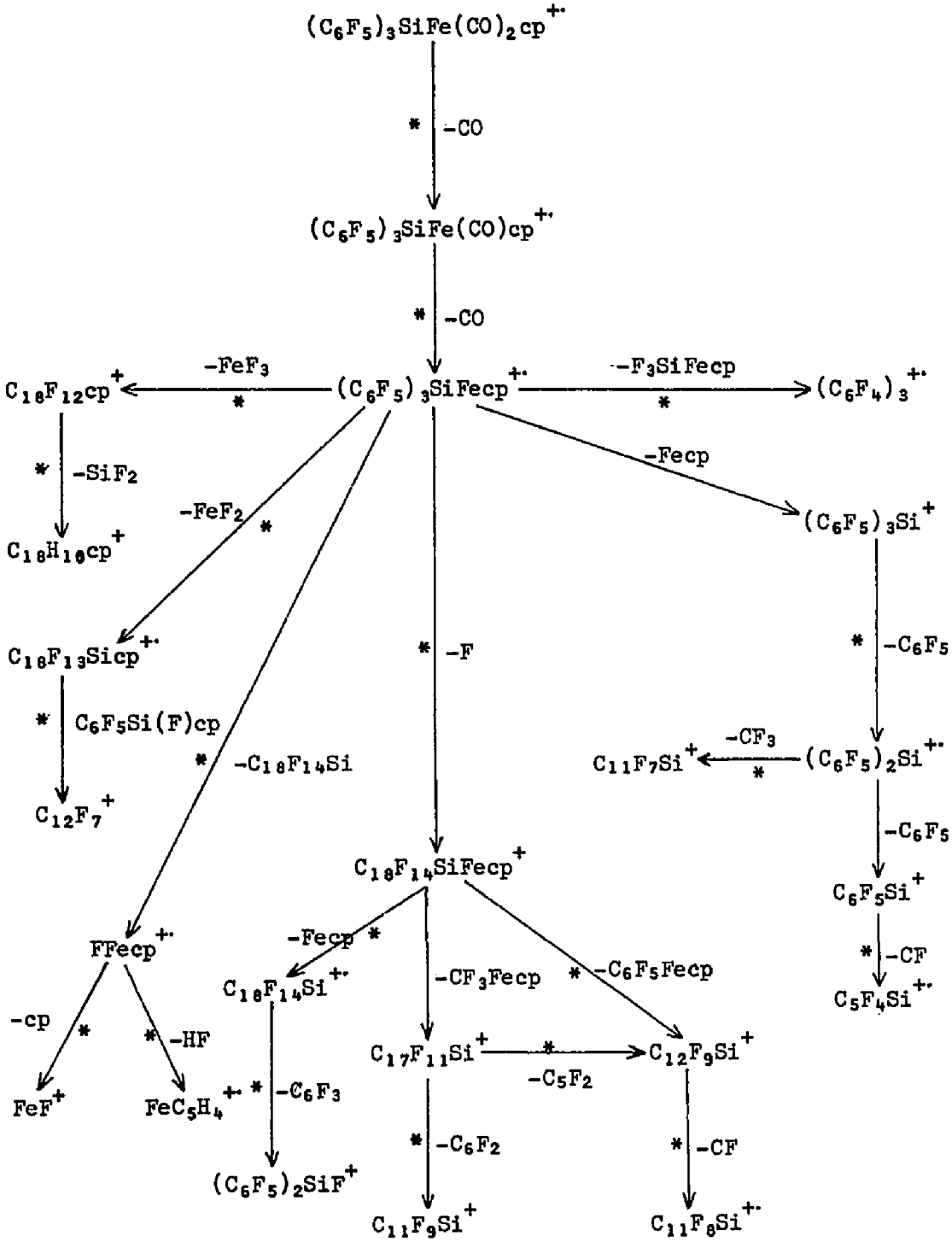


Figure 4-11

Partial Fragmentation Pattern for $(C_6F_5)_3GeFe(CO)_2cp$

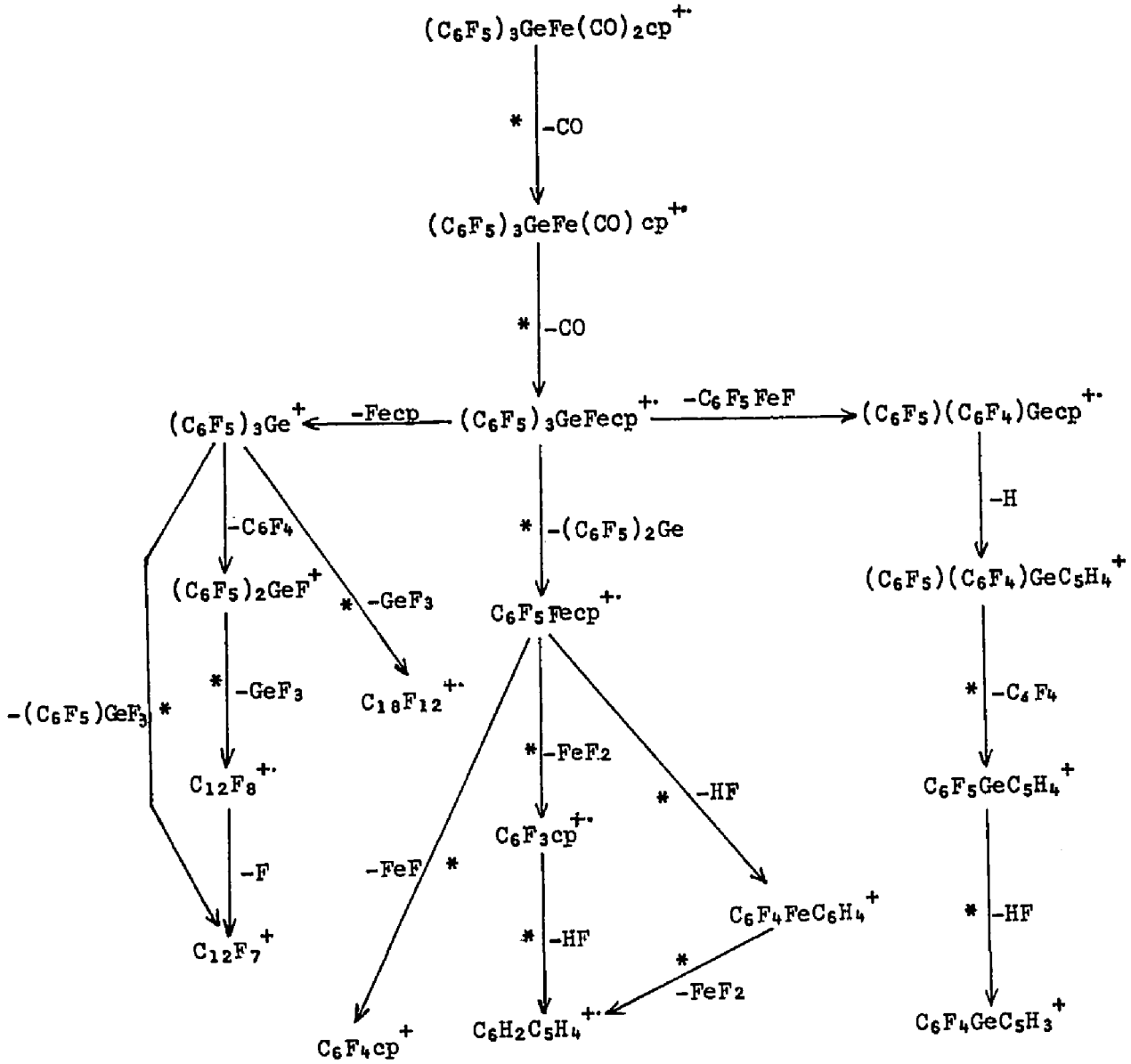


Figure 4-12

Partial Fragmentation Pattern for $(C_6F_5)_3SnFe(CO)_2cp$

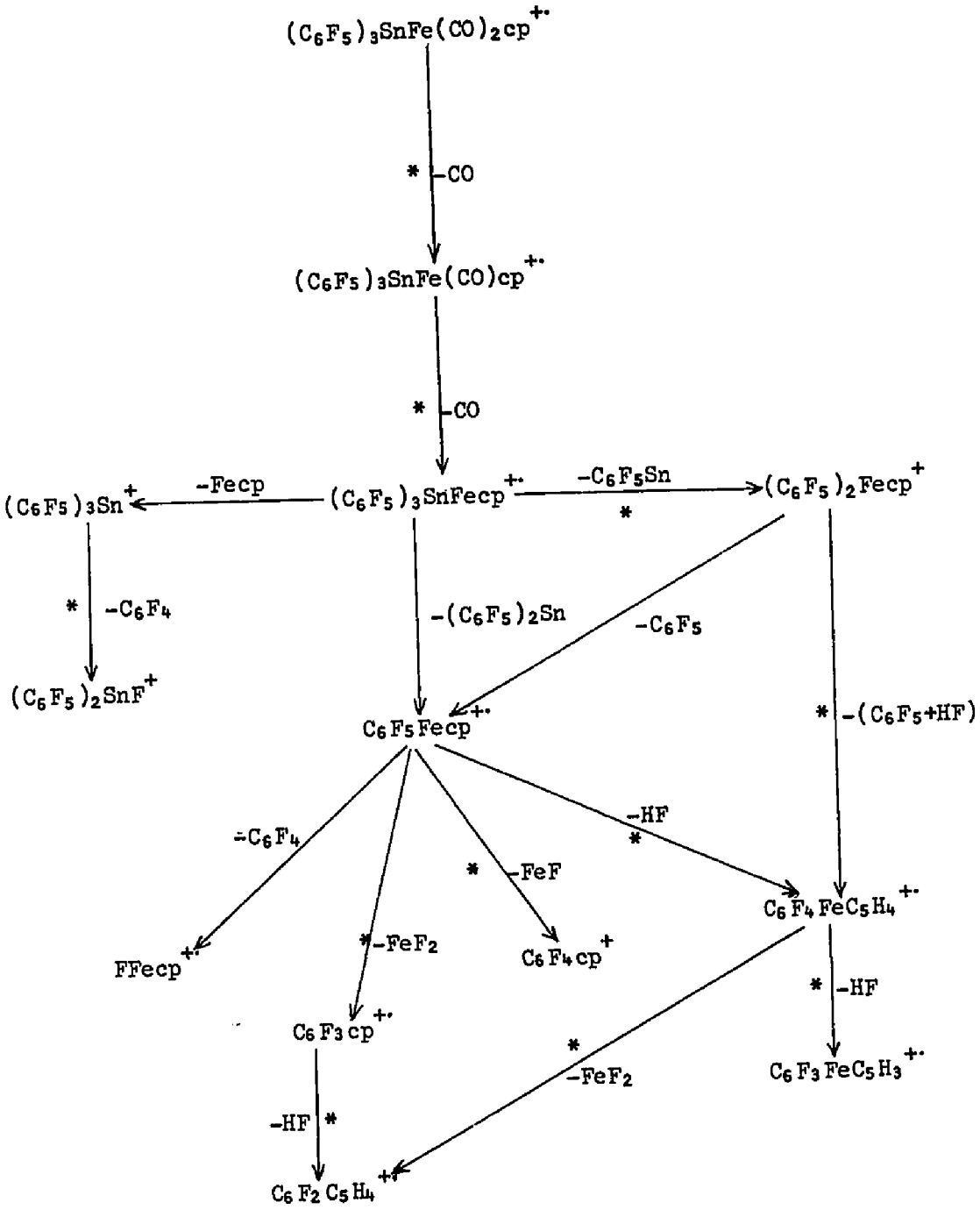


Figure 4-13

		m* calc.	m* found
$Ph_2(C_6F_5)MMn(CO)_5^+ \rightarrow Ph_2(C_6F_5)MMn(CO)_4^+ + CO$	M=Si	489.4	489.0
	M=Ge	535.5	535.0
	M=Sn	581.2	581.5
$Ph_2(C_6F_5)Mn(CO)_5^+ \rightarrow Ph_2(C_6F_5)M^+ + Mn(CO)_5$	M=Si	223.9	224.0
	M=Ge	264.4	264.0
	M=Sn	305.8	306.0
$Ph_2(C_6F_5)MMn^+ \rightarrow Ph_2(C_6F_5)M + Mn$	M=Si	301.5	301.5
	M=Ge	354.6	355.0

The silicon derivative was the only one to show the loss of more than one carbonyl group or the loss of a manganese carbonyl species containing less than five carbonyl groups; both these transition occuring from the ion $Ph_2(C_6F_5)SiMn(CO)_2^+$.

	m* calc.	m* found
$Ph_2(C_6F_5)SiMn(CO)_2^{+\cdot} \rightarrow Ph_2(C_6F_5)SiMn^{+\cdot} + 2CO$	354.8	355.0
$Ph_2(C_6F_5)SiMn(CO)_2^{+\cdot} \rightarrow Ph_2(C_6F_5)Si^+ + Mn(CO)_2$	264.8	265.0

As before, the silicon derivative fragments in a substantially different way to the germanium and tin compounds, and as in the hydrocarbon derivatives, loses benzene or hydrogen from the ion $Ph_2(C_6F_5)Si^+$, although the loss of PhSi is also observed.

	m* calc.	m* found
$Ph_2(C_6F_5)Si^+ \rightarrow (C_6H_4)_2SiC_6F_5^+ + H_2$	334.7	335.0
$Ph_2(C_6F_5)Si^+ \rightarrow C_6F_4(C_6H_4)SiF^+ + C_6H_6$	210.4	210.0
$Ph_2(C_6F_5)Si^+ \rightarrow C_6F_5C_6H_5^{+\cdot} + PhSi$	170.6	170.5

Several fragmentation routes characteristic of a fluorocarbon

derivative are also observed

	m* calc.	m* found
$Ph_2(C_6F_5)Si^+ \rightarrow C_{18}F_2H_{10}^{+\cdot} + SiF_3$	199.7	200.0
$Ph_2(C_6F_5)Si^+ \rightarrow Ph_2SiF^+ + C_6F_4$	115.8	116.0

as well as the loss of HF,

	m* calc.	m* found
$Ph_2SiF^+ \rightarrow C_{12}H_9Si^+ + HF$	163.0	163.0

In the mass spectra of the tin and germanium derivatives the major mode of fragmentation of the $Ph_2(C_6F_5)M^+$ ion is not by the loss of C_6F_4 observed for the silicon derivative, but rather by the loss of PhC_6F_5 to give the PhM^+ ion although none of the appropriate metastable transitions were observed. However, in both derivatives the loss of C_6F_4 does occur to some extent and is supported by the metastable transitions.

		m* calc.	m* found
$Ph_2(C_6F_5)M \rightarrow Ph_2MF + C_6F_4$	M = Ge	154.5	154.0
	M = Sn	194.7	195.0

There is no evidence that the loss of hydrogen, benzene, PhM or a metal fluoride species occurs to any appreciable extent in either of these compounds although the tin derivative did show the loss of HF from the very weak ion $Ph_2(C_6F_5)Sn^+$.

	m* calc.	m* found
$Ph_2(C_6F_5)Sn^+ \rightarrow Ph(C_6F_4)(C_6H_4)Sn^+ + HF$	401.9	402.0

As in the case of the $Ph_3SnMn(CO)_5$ derivatives, fragmentation of the $Ph_2(C_6F_5)MMn^{+\cdot}$ ion can occur before the metal-metal bond is

broken, such that the ion $Ph_2(C_6F_5)SnMn^{+\cdot}$ was observed to lose C_6F_4 to give the ion $Ph_2Sn(F)Mn^{+\cdot}$,

	m* calc.	m* found
$Ph_2(C_6F_5)SnMn^{+} \rightarrow Ph_2Sn(F)Mn^{+} + C_6F_4$	244.2	244.0

while the analogous germanium ion showed its subsequent fragmentation to the $PhGe^{+}$ ion by the loss of PhMnF.

	m* calc.	m* found
$Ph_2Ge(F)Mn^{+\cdot} \rightarrow PhGe^{+} + PhMnF$	75.5	75.6

Since the abundances and ion types are very comparable for the germanium and tin derivatives, these processes probably occur to an equal extent in both compounds, but only the germanium derivative showed the alternative fragmentation process.

	m* calc.	m* found
$Ph_2Ge(F)Mn^{+\cdot} \rightarrow FGeMn^{+\cdot} + Ph_2$	72.5	72.5

The substantial distinction between the silicon and the germanium or tin derivatives is again emphasised by noting that there are no ions of the type $Ph_2Si(F)Mn^{+\cdot}$ present in the spectrum of the silicon derivative. This can be attributed to a higher M-C bond strength in the silicon derivative so that the Si-Mn bond will be cleaved preferentially over the silicon-carbon bond. The unusually stable PhM^{+} ion undergoes the same fragmentation route as that described previously for these ions; the $PhGe^{+}$ ion losing acetylene to give $C_4H_3Ge^{+}$, while the $PhSn^{+}$ ion preferentially loses a phenyl radical to give the tin ion

	m* calc.	m* found
$PhGe^{+} \rightarrow C_4H_3Ge^{+} + C_2H_2$	103.5	103.4

	m* calc.	m* found
$PhSn^+ \rightarrow Sn^+ + Ph$	73.0	73.0

For both the silicon and germanium derivatives the loss of a fluorine radical occurs from the ion $Ph_2(C_6F_5)M$, and in the spectra of the germanium derivative its subsequent fragmentation by loss of PhGeF was observed.

	m* calc.	m* found
$Ph_2(C_6F_4)Ge^{+\cdot} \rightarrow C_{12}F_3H_5^{+\cdot} + PhGeF$	113.5	113.5

8) The $Ph_2(C_6F_5)MFe(CO)_2cp$ Derivatives (M = Si or Sn)

The relative abundances and proposed fragmentation patterns for these derivatives are given in Table 4-6 and Figures 4-17 to 18 respectively. Metastable transitions due to the loss of a carbonyl group were observed in both cases, although the spectra of the tin derivative was the only one to show the loss of both carbonyls successively.

	m* calc.	m* found
$Ph_2(C_6F_5)SiFe(CO)cp^{+\cdot} \rightarrow Ph_2(C_6F_5)SiFecp^{+\cdot} + CO$	443.5	443.5
$Ph_2(C_6F_5)SnFe(CO)_2cp^{+\cdot} \rightarrow Ph_2(C_6F_5)SnFe(CO)cp^{+\cdot} + CO$	563.3	563.5
$Ph_2(C_6F_5)SnFe(CO)cp^{+\cdot} \rightarrow Ph_2(C_6F_5)SnFecp^{+\cdot} + CO$	535.3	535.0

However, unlike the $Ph_3MFe(CO)_2cp$ derivatives, the loss of $Fe(CO)_2cp$ from the molecular ion or Fecp from the ion $Ph_2(C_6F_5)MFecp^{+\cdot}$ was not observed in either case, although the abundances of the $Ph_2(C_6F_5)M^+$ ion indicate that this process must occur to some extent, especially in the tin derivative. Both spectra showed ions that were due to the loss of a phenyl group, but while the origin of the $Ph(C_6F_5)SiFecp^+$ ion was not determined, the tin derivative showed via the appropriate

Table 4-5

The 70 e.v. Mass Spectra of the Compounds $Ph_2(C_6F_5)MMn(CO)_5$

Ion M =	Relative Abundance % Si	Ge	Sn
a) Ions containing two metals:			
$Ph_2(C_6F_5)MMn(CO)_5^{+\cdot}$	1.5	0.4	2.0
$Ph_2(C_6F_5)MMn(CO)_4^{+\cdot}$	1.5	0.4	1.0
$Ph_2(C_6F_5)MMn(CO)_2^{+\cdot}$	6.8	7.9	6.7
$Ph_2(C_6F_5)MMn^{+\cdot}$	6.8	7.9	6.7
$Ph_2(F)MMn^{+\cdot}$		4.0	2.1
$Ph(F)MMn^{+}$		0.2	
$FMMn^{+\cdot}$	a)		b)
b) Ions containing one metal:			
$Ph_2(C_6F_5)M^{+}$	12.6	17.4	20.6
$C_{18}H_9F_5M^{+\cdot}$	0.6		
$C_{18}F_8F_5M^{+}$	0.1		
$C_{18}H_{10}F_4M^{+\cdot}$		0.5	
$Ph(C_6F_5)MF^{+}$		3.5	1.0
$Ph(C_6F_5)M^{+\cdot}$	0.6		
$C_{12}F_5H_4M^{+}$	1.2		
$C_{12}F_4H_4M^{+\cdot}$			0.4
Ph_2MF^{+}	16.4	5.2	1.9
$C_{12}H_9MF^{+\cdot}$	0.3		
$C_{12}H_8MF^{+}$	1.6		
$C_{12}H_7MF^{+\cdot}$	0.2		
$Ph_2M^{+\cdot}$		0.7	0.1

a) Overlapped by C_6F_4 and $PhGe^{71+}$
b) Overlapped by $PhSn^{115+}$

Table 4-5 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_{12}H_9M^+$	0.9	0.7	0.3
$C_{10}H_7M^+$	0.3		
$C_8H_5M^+$	0.3		
PhM^+	1.6	22.7	26.5
$C_6H_3M^+$	0.3		
$C_4H_3M^+$	0.6	2.4	0.5
C_2HM^+			0.2
MF^+	4.0	3.8	4.5
$M^{+\cdot}$			4.4
$Mn(CO)_5^+$	0.1	0.2	0.4
$Mn(CO)_4^+$	0.4	0.2	0.3
$Mn(CO)_3^+$	0.2	0.2	c)
$Mn(CO)_2^+$	0.4	0.3	0.5
$MnCO^+$	0.7	0.8	0.8
Mn^+	6.3	5.8	3.6
MnF_2^+	0.2		
$MnF^{+\cdot}$	1.6	1.6	0.9
$PhMn^{+\cdot}$	0.7	1.1	0.6
$C_6F_5Mn^{+\cdot}$		0.2	0.2
$HMn^{+\cdot}$	0.4	0.2	0.2
c) Hydrocarbon/fluorocarbon ions:			
$C_{18}F_2H_{10}^{+\cdot}$	2.0		
$PhC_6F_5^{+\cdot}$	1.9	1.0	0.2
$(C_6F_4)(C_6H_4)^{+\cdot}$	1.0		

c) overlapped with $Sn^{120}F^+$

Table 4-5 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_{12}F_3H_5^{+\cdot}$	0.4		
$C_{12}F_2H_5^{+}$	1.2		
$Ph_2^{+\cdot}$	0.5	0.1	0.5
$(C_6H_4)_2^{+\cdot}$	0.5		0.2
$C_6F_5H^{+\cdot}$	1.0	0.7	1.9
$C_6F_5^{+}$ d)			
$C_6F_4H^{+}$	0.6		0.3
$C_6F_4^{+\cdot}$	0.1	0.2	0.3
$C_5F_2H^{+\cdot}$	0.7	0.6	0.9
$C_5F^{+\cdot}$	0.6	0.1	
$C_6H_6^{+\cdot}$	0.6	0.3	2.1
Ph^{+}	3.1	2.4	1.7
$C_4H_3^{+}$	1.8	1.6	1.7
$C_4H_2^{+\cdot}$	0.4	0.4	0.2

d) overlapped with $Mn(CO)_4^{+}$

Partial Fragmentation Pattern for $Ph_2(C_6F_5)SiMn(CO)_5$

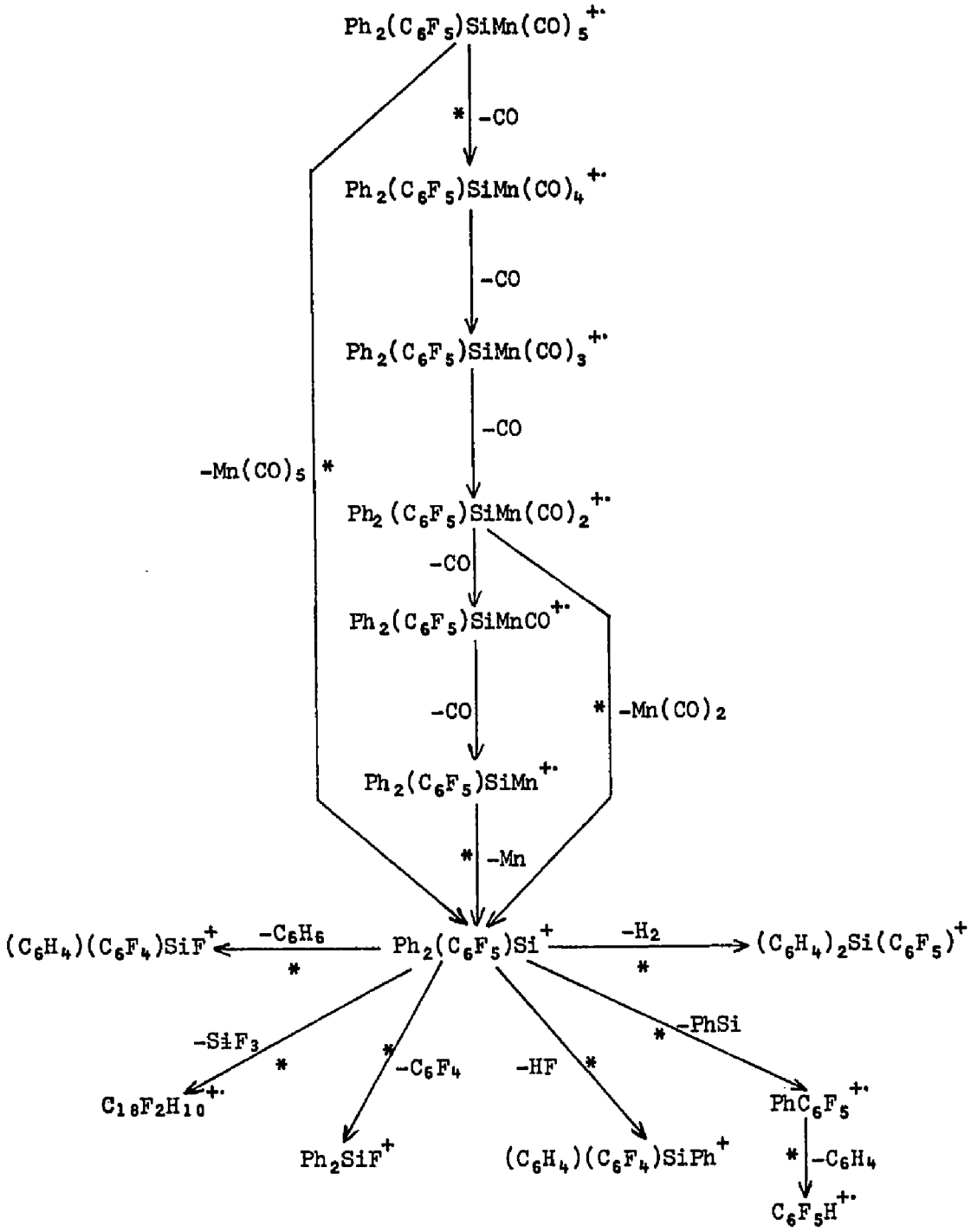


Figure 4-14

Partial Fragmentation Pattern for $Ph_2(C_6F_5)GeMn(CO)_5$

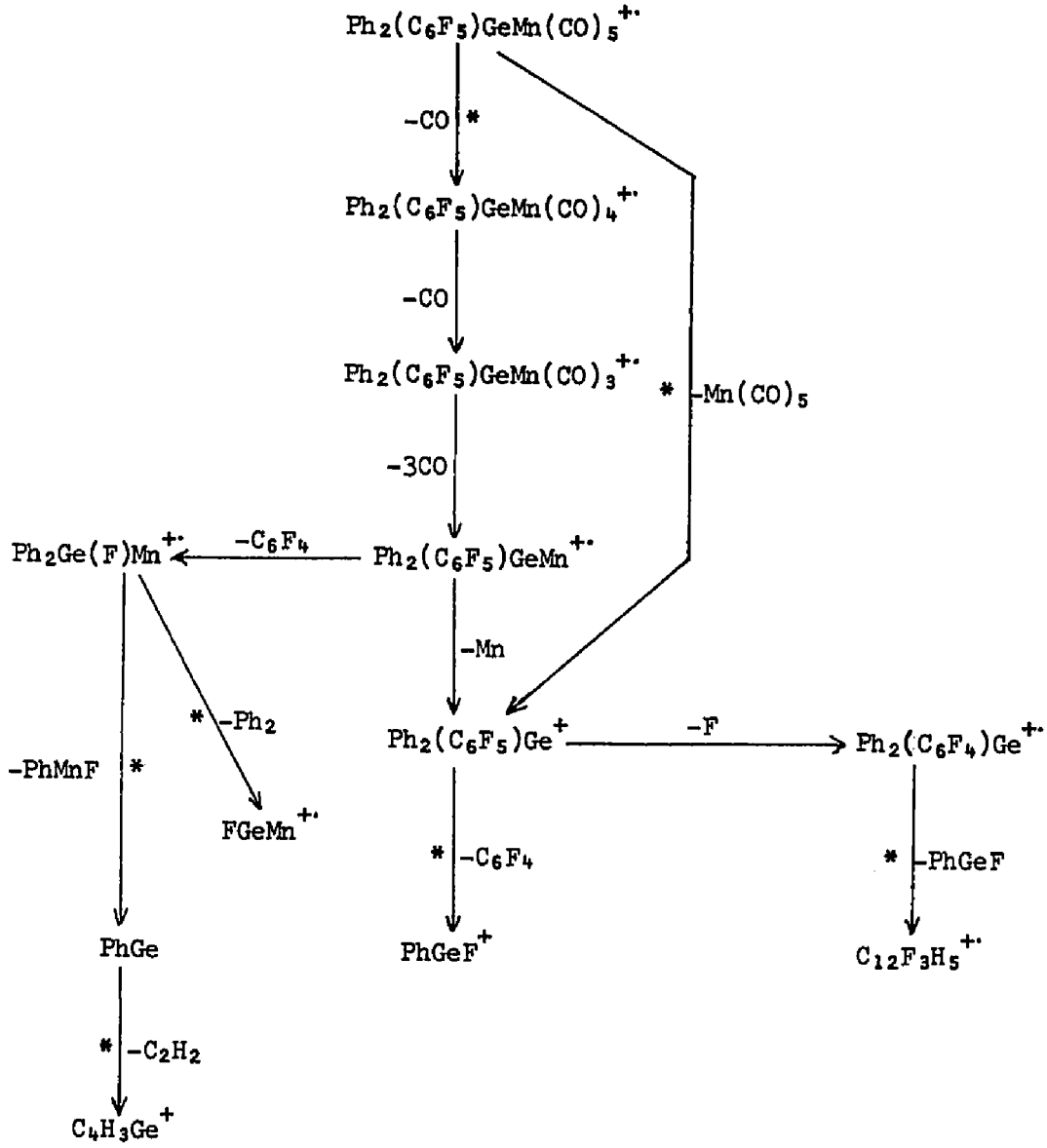


Figure 4-15

Partial Fragmentation Pattern for $Ph_2(C_6F_5)SnMn(CO)_5$

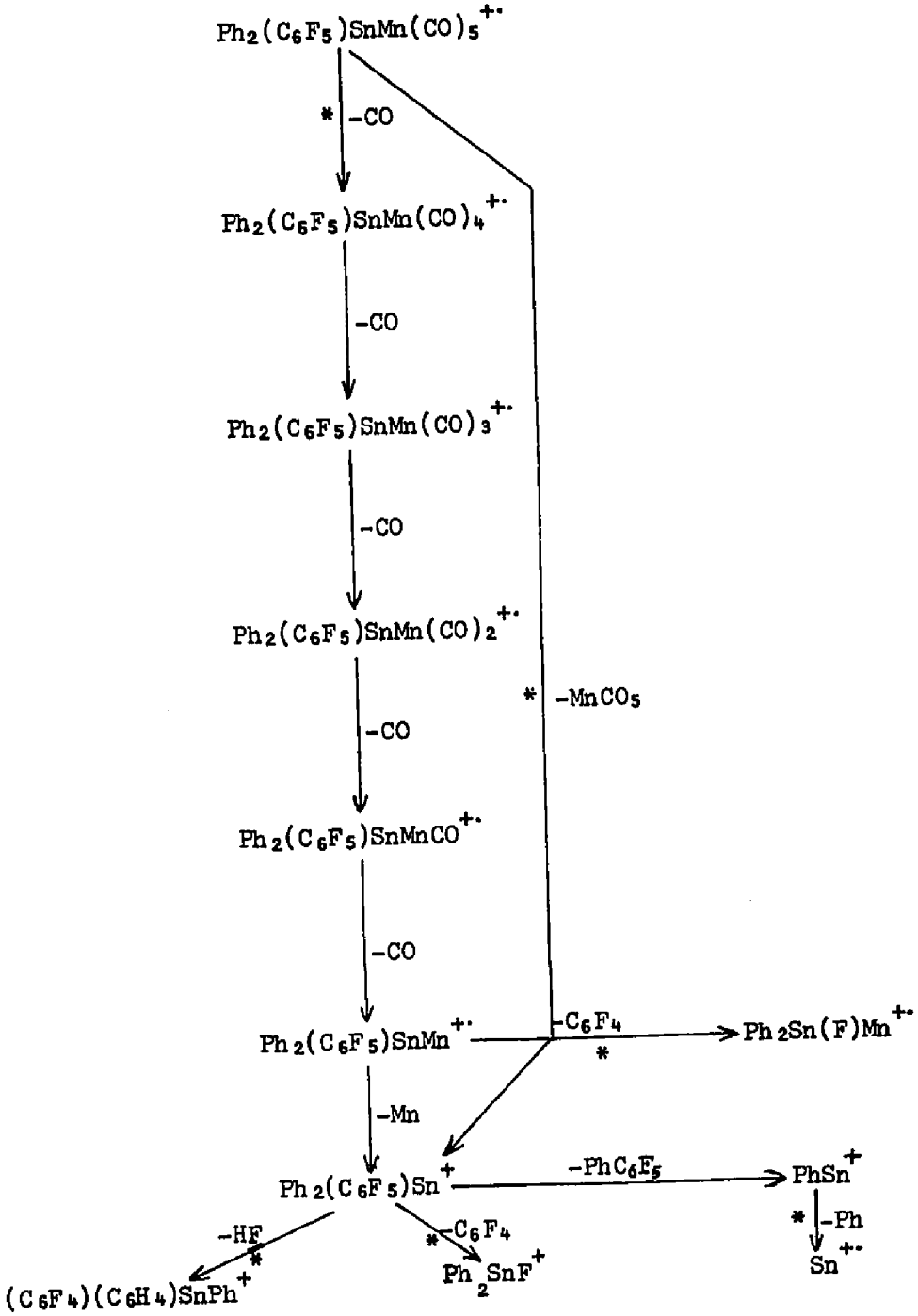


Figure 4-16

transitions that this could occur from any member of the ion series $Ph_2(C_6F_5)SnFe(CO)_ncp^{+\cdot}$ (n = 0 to 2).

	m* calc.	m* found
$Ph_2(C_6F_5)SnFe(CO)_2cp^{+\cdot} \rightarrow Ph(C_6F_5)SnFe(CO)_2cp^{+} + Ph$	473.6	474.0
$Ph_2(C_6F_5)SnFe(CO)cp^{+\cdot} \rightarrow Ph(C_6F_5)SnFecp^{+} + PhCO$	398.7	399.0
$Ph_2(C_6F_5)SnFecp^{+\cdot} \rightarrow Ph(C_6F_5)SnFecp^{+} + Ph$	418.5	419.0

By contrast the metastable supported loss of a C_6F_5 group from ions of this type is not observed, although this process must occur in the spectra of the tin derivative to form the ion $Ph_2SnFecp^{+}$.

As in the spectrum of $Ph_3SiFe(CO)_2cp$, extensive loss of a hydrogen radical or molecule took place from the $Ph_2(C_6F_5)SiFecp^{+\cdot}$ ion, but as in the case of the manganese pentacarbonyl derivative the majority of the ions in the spectrum are derived from the $Ph_2(C_6F_5)Si^{+}$ ion, which fragments in an exactly analogous way to that described previously to give the Ph_2SiF^{+} ion as the base peak. The Ph_2SiF^{+} ion was observed to fragment by the loss of HF and H_2 to give the ions $(C_6H_4)_2SiH^{+}$ and $(C_6H_4)_2SiF^{+}$ respectively,

	m* calc.	m* found
$Ph_2SiF^{+} \rightarrow (C_6H_4)_2SiF^{+} + H_2$	197.0	197.0
$Ph_2SiF^{+} \rightarrow (C_6H_4)_2SiH^{+} + HF$	163.0	163.0

which fragments further to give $C_{10}H_7Si^{+}$ or $(C_6H_4)_2^{+}$ by loss of acetylene or SiF.

	m* calc.	m* found
$(C_6H_4)_2SiF^{+} \rightarrow (C_6H_4)_2^{+\cdot} + SiF$	116.1	116.0
$(C_6H_4)_2SiH^{+} \rightarrow C_{10}H_7Si^{+} + C_2H_2$	132.7	132.8

Although these transitions were not observed in the mass spectrum of $Ph_2(C_6F_5)SiMn(CO)_5$, they probably occur to a very similar extent, since in both spectra, the ions containing only silicon show a similar abundance.

In the spectrum of the tin derivative, more rearrangement ions are observed and give rise to ions of the type Ph_2Fecp^+, $PhFecp^{+\cdot}$, and cpM^+ , all of which are absent from the spectrum of the silicon derivative. As in the other tin iron derivatives, ions containing a metal-metal bond play a more important role in the fragmentation pattern than for their silicon and germanium analogues. The ion $Ph_2(C_6F_5)\ Sn^+$ is however still quite abundant and fragments by the loss of C_6F_4, as would be expected.

	m* calc.	m* found
$Ph_2(C_6F_5)Sn^+ \rightarrow Ph_2SnF^+ + C_6F_4$	194.7	195.0

However, although the loss of PhC_6F_5 is just as likely to give the very abundant ion $PhSn^+$, this was not observed.

The ion $Ph(C_6F_5)SnFecp^+$ was also observed to fragment by loss of C_6F_4 to give the ion $PhSn(F)Fecp^+$ which then further loses PhFeF.

	m* calc.	m* found
$Ph(C_6F_5)SnFecp^+ \rightarrow Ph(F)SnFecp^+ + C_6F_4$	234.2	234.2
$Ph(F)SnFecp^+ \rightarrow cpSn^+ + PhFeF$	102.2	102.0

The characturistic loss of acetylene from Ph_2Fecp^+, and the loss of a phenyl group from Ph_2Sn^+ were also observed.

	m* calc.	m* found
$PhFecp^+ \rightarrow PhFeC_3H_3^+ + C_2H_2$	149.4	149.6
$Ph_2Sn^{+\cdot} \rightarrow PhSn^+ + Ph$	141.8	141.7

Table 4-6

The 70 e.v. Mass Spectra of the Compounds $Ph_2(C_6F_5)MFe(CO)_2cp$

Ion M =	Relative Abundance % Si	Sn
a) Ions containing two metals:		
$Ph_2(C_6F_5)MFe(CO)_2cp^{+\cdot}$	0.1	1.8
$Ph_2(C_6F_5)MFe(CO)cp^{+\cdot}$	1.6	4.8
$Ph_2(C_6F_5)MFecp^{+\cdot}$	7.9	3.7
$C_{23}H_{14}F_5MFe^{+}$	3.3	
$C_{23}H_{12}F_5MFe^{+}$	0.3	
$C_{23}H_{15}F_4MFe^{+}$	0.1	
$Ph(C_6F_5)MFe(CO)_2cp^{+}$	0.1	0.3
$Ph(C_6F_5)MFecp^{+}$	0.3	6.0
Ph_2MFecp^{+}		1.1
$Ph(F)MFecp^{+}$	0.5	1.6
$PhMFecp^{+\cdot}$	1.3	
$(C_6H_4)_2MFecp^{+}$	0.5	0.1
$C_{11}H_9MFe^{+}$	1.0	
$C_{11}H_8MFe^{+\cdot}$	0.9	
$C_{11}H_7MFe^{+}$	0.4	
$M-Fe^{+\cdot}$		0.1
b) Ions containing one metal:		
$Ph_2(C_6F_5)M^{+}$	1.4	9.5
Ph_3M^{+} a)		3.4
Ph_2MF^{+}	10.0	3.0
$C_{12}H_9MF^{+\cdot}$	0.4	

a) Ion formed by ion-molecule reaction

Table 4-6 cont'd

Ion M =	Relative Abundance % Si	Sn
$C_{12}H_8MF^+$	2.9	
$Ph_2M^{+\cdot}$	0.1	
$C_{12}H_9M^+$	1.8	
$C_{12}H_8M^{+\cdot}$	0.5	
$C_{11}H_9M^+$	0.3	
$C_{10}H_7M^+$	0.6	
$C_8H_5M^+$	0.3	
PhM^+	1.5	9.5
$C_6H_3M^+$	0.2	
cpM^+		4.4
MF^+	2.9	4.9
$M^{+\cdot}$		4.1
Ph_2Fecp^+		0.7
$Fe(CO)_2cp^+$	0.2	0.3
$FFe(CO)cp^{+\cdot}$ b)		
$Fe(CO)cp^+$	1.0	0.6
$PhFecp^{+\cdot}$		4.3
$C_{11}H_8Fe^{+\cdot}$	0.3	2.0
$FFecp^{+\cdot}$	0.3	0.2
$Fecp^+$	4.2	4.0
$C_3H_3Fe^+$	0.6	0.6
FeF^+	0.3	
$Fe^{+\cdot}$	3.9	2.9

b) Overlapped with $C_6F_5H^{+\cdot}$

Table 4-6 cont'd

	Ion M =	Relative Abundance % Si	Sn
c)	Hydrocarbon/fluorocarbon Ions		
	$PhC_6F_5^{+\cdot}$	3.8	
	$C_6F_5C_6H_4^{+}$	0.8	
	$C_6F_4C_6H_4^{+\cdot}$	0.7	
	$C_6F_5H^{+\cdot}$	0.7	1.4
	$C_6F_5^{+}$	0.6	
	$Ph_2^{+\cdot}$	0.3	0.2
	$Phcp^{+\cdot}$	0.3	1.7
	$(C_6H_4)_2^{+\cdot}$	0.9	0.2
	$C_5F_2H^{+}$	0.6	0.4
	$C_6H_6^{+\cdot}$	0.2	0.8
	Ph^{+}	2.6	1.7
	$C_4H_3^{+}$	0.1	1.1
	$C_4H_2^{+\cdot}$		0.3

Partial Fragmentation Pattern for $Ph_2(C_6F_5)SiFe(CO)_2cp$

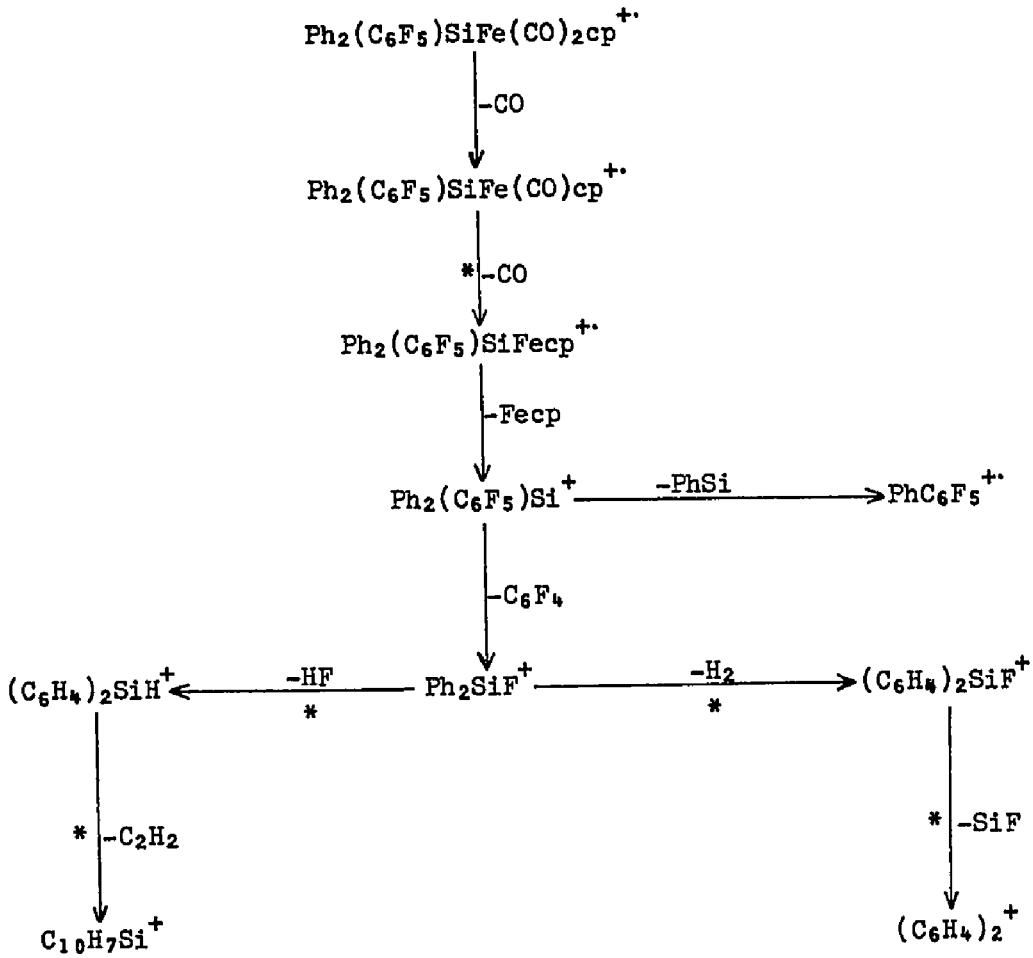


Figure 4-17

Partial Fragmentation Pattern for $Ph_2(C_6F_5)SnFe(CO)_2cp$

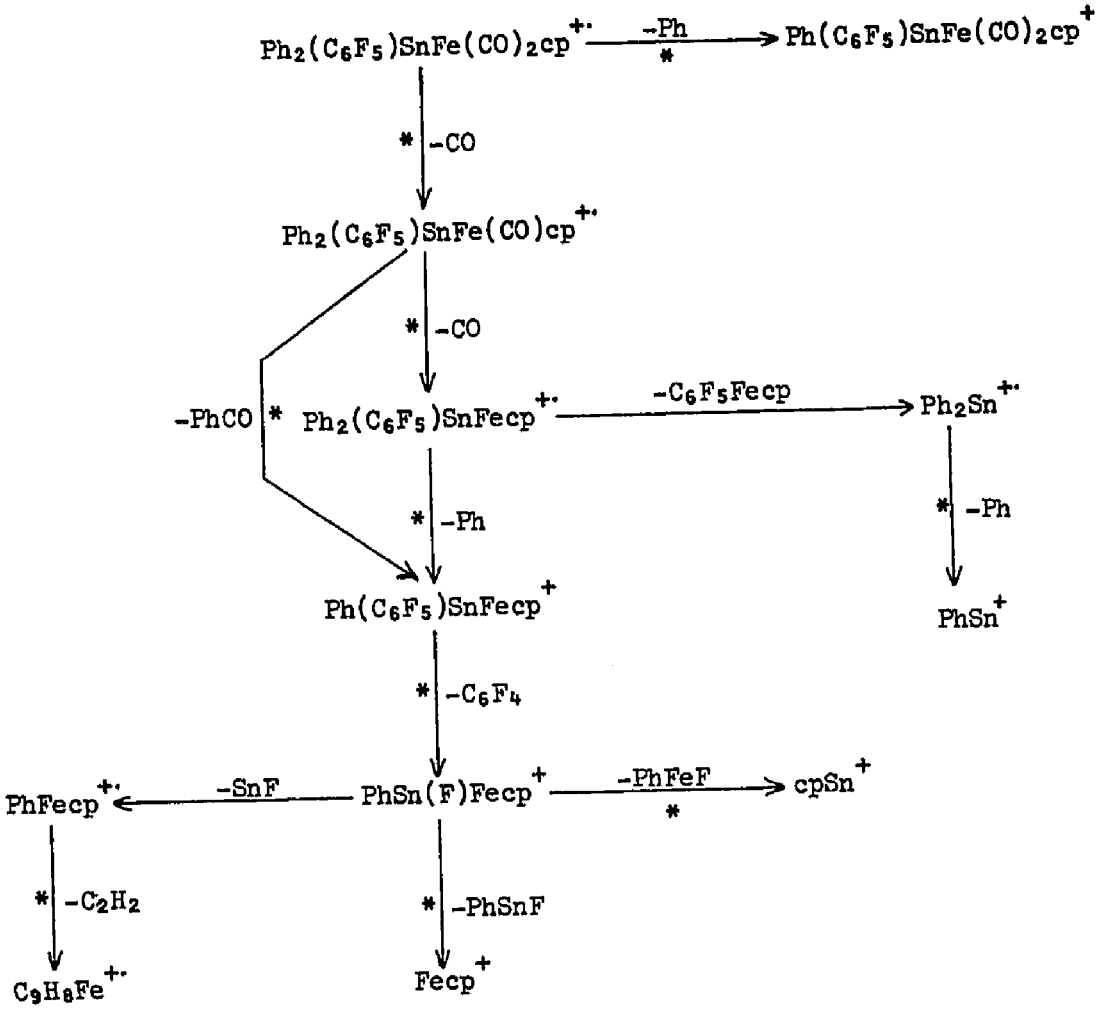


Figure 4-18

9) The $Ph(C_6F_5)_2MMn(CO)_5$ Derivatives

The relative abundances and fragmentation patterns for these compounds are shown in Table 4-7 and Figures 4-19 to 21. As might be expected, the spectrum of the silicon compound is characterised by a very complex fragmentation pattern that gives rise to a large number of ions that contain just carbon hydrogen and fluorine. There is once again a distinct contrast between the mass spectrum of this compound and those of the germanium and tin derivatives, since in the latter cases the abundances of the non-metal containing ions are very low and the spectrum completely dominated by the PhM^+ ions.

As in the tris(pentafluorophenyl) derivatives the initial loss of one carbonyl group is always observed along with the loss of one or more carbonyl groups from the series $Ph(C_6F_5)_2MMn(CO)_n^{+\cdot}$ (n = 0 to 4)

		m* calc.	m* found
$Ph(C_6F_5)_2MMn(CO)_5^{+\cdot} \rightarrow Ph(C_6F_5)_2MMn(CO)_4^{+\cdot} + CO$	M = Si	579.2	570.0
	M = Ge	625.2	625.0
	M = Sn	671.1	671.0
$Ph(C_6F_5)_2SiMn(CO)_4^{+\cdot} \rightarrow Ph(C_6F_5)_2SiMn(CO)_2^{+\cdot} + 2CO$		499.2	499.0
$Ph(C_6F_5)_2SiMn(CO)_2^{+\cdot} \rightarrow Ph(C_6F_5)_2SiMn^{+\cdot} + 2CO$		443.7	443.5
$Ph(C_6F_5)_2SiMn(CO)_2^{+\cdot} \rightarrow Ph(C_6F_5)_2SiMnCO^{+\cdot} + CO$		495.0	495.4
$Ph(C_6F_5)_2SiMnCO^{+\cdot} \rightarrow Ph(C_6F_5)_2SiMn^{+\cdot} + CO$		467.5	468.0
$Ph(C_6F_5)_2GeMn(CO)_4^{+\cdot} \rightarrow Ph(C_6F_5)_2GeMn^{+\cdot} + 4CO$		447.2	447.0
$Ph(C_6F_5)_2SnMn(CO)_4^{+\cdot} \rightarrow Ph(C_6F_5)_2SnMn(CO)_3^{+\cdot} + CO$		643.0	643.0

The metastable supported loss of a manganese atom from the $Ph(C_6F_5)_2MMn^{+\cdot}$ ion, or the loss of $Mn(CO)_5$ from the molecular ion was not observed in any of the three spectra although it must occur to an

appreciable extent, since the abundances of the ions $Ph(C_6F_5)_2M$ are quite large. The tin derivative did however show the transition

	m* calc.	m* found
$Ph(C_6F_5)_2SnMn(CO)_4^{+\cdot} \rightarrow Ph(C_6F_5)_2Sn^+ + Mn(CO)_4$	492.0	492.0

The silicon derivative showed the expected loss of silicon and manganese fluorides from the ion $Ph(C_6F_5)_2SiMn^{+\cdot}$.

	m* calc.	m* found
$Ph(C_6F_5)_2SiMn^{+\cdot} \rightarrow (C_6F_5)_2Mn^+ + PhSiF_2$	249.3	249.0
$\rightarrow C_{18}F_7H_5Si^+ + MnF_3$	295.4	295.0
$\rightarrow C_{18}F_5H_5^{+\cdot} + SiF_3 + MnF_2$	202.1	202.4
$\rightarrow Ph(C_6F_6)_2Si^+ + MnF_2$	325.5	326.0

and the ions $Ph(C_6F_4)_2Si^+$ and $C_{12}F_3H_5Si^{+\cdot}$ also showed the characteristic elimination of silicon fluorides.

	m* calc.	m* found
$Ph(C_6F_4)_2Si^+ \rightarrow C_{18}F_5H_5^{+\cdot} + SiF_3$	218.6	219.0
$C_{12}F_3H_5Si^{+\cdot} \rightarrow C_{12}F_2H_5^+ + SiF$	149.4	149.0

Unlike most other silicon derivatives, the loss of PhSi, Ph and $Ph(C_6F_5)Si$ were also observed and are rather unusual, since these types of fragmentation are in general more characteristic of the heavier members of Group IV (38, 183).

	m* calc.	m* found
$Ph(C_6F_5)_2Si^+ \rightarrow (C_6F_5)_2Si^{+\cdot} + Ph$	298.5	298.0
$Ph(C_6F_4)_2Si^+ \rightarrow C_6F_3^+ + C_6F_5SiPh$	41.5	41.5
$\rightarrow (C_6F_4)_2^{+\cdot} + PhSi$	218.6	219.0

The abundance of the $C_6F_5Mn^+$ ion in this spectrum was virtually zero,

the only other fluorocarbon manganese ion being $(C_6F_4)_2Mn^+$, which was observed to fragment by loss of manganese or manganese fluoride.

	m* calc.	m* found
$(C_6F_4)_2Mn^+ \rightarrow (C_6F_4)_2^{+\cdot} + Mn$	249.6	249.0
$(C_6F_4)_2Mn^+ \rightarrow C_{12}F_7^+ + MnF$	218.6	219.0

The spectra of the germanium and tin derivatives are very comparable, and by far the most important fragmentation mode is by the loss of $(C_6F_5)_2$ from the ion $Ph(C_6F_5)_2M^+$, or by the loss of $(C_6F_5)_2Mn$ from the ion $Ph(C_6F_5)_3MMn^{+\cdot}$, to give the very intense PhM^+ ion which fragments as previously described.

	m* calc.	m* found
$Ph(C_6F_5)_2Sn^+ \rightarrow PhSn^+ + (C_6F_5)_2$	73.1	73.0
$Ph(C_6F_5)_2GeMn^+ \rightarrow PhGe^+ + (C_6F_5)_2Mn$	42.0	42.0

Even though only one metastable transition was observed for each derivative, it is quite probable that both processes occur to an equal extent in each, since the abundances of the parent and daughter fragment ions do not seem to vary appreciably.

As for the other pentafluorophenyl derivatives of tin and germanium, the characteristic loss of C_6F_4 was observed, and for the tin derivative the ion $Ph(C_6F_5)_2Sn^+$ was shown to fragment by loss of PhSnF and PhF.

		m* calc.	m* found
$Ph(C_6F_5)_2M^+ \rightarrow Ph(C_6F_5)MF^+ + C_6F_4$	M = Ge	234.2	234.0
	M = Sn	276.2	276.3
$C_6F_5Sn^+ \rightarrow SnF^+ + C_6F_4$		67.3	67.2

	m* calc.	m* found
$Ph(C_6F_5)SnF^+ \rightarrow C_6F_5^+ + PhSnF$	72.8	73.0
$Ph(C_6F_5)SnF^+ \rightarrow C_6F_5Sn^+ + PhF$	338.5	338.4

This last transition is quite rare for these and other phenyl pentafluorophenyl derivatives of Group IV (183).

10) The $Ph(C_6F_5)_2MFe(CO)_2cp$ Derivatives (M = Si or Sn)

The ion abundances and proposed fragmentation pattern for these derivatives are given in Table 4-8 and Figures 4-22 to 23 respectively. While the silicon derivative showed only the loss of one carbonyl group, the tin derivative showed the loss of both groups, as well as the simultaneous loss of both carbonyl groups from ions formed by the loss of phenyl or C_6F_5 from the molecular ion.

	m* calc.	m* found
$Ph(C_6F_5)_2SiFe(CO)cp^{+\cdot} \rightarrow Ph(C_6F_5)_2SiFecp^{+\cdot} + CO$	533.3	533.0
$Ph(C_6F_5)_2SnFe(CO)_2cp^{+\cdot} \rightarrow Ph(C_6F_5)_2SnFe(CO)cp^{+\cdot} + CO$	653.1	653.0
$Ph(C_6F_5)_2SnFe(CO)cp^{+\cdot} \rightarrow Ph(C_6F_5)_2SnFecp^{+\cdot} + CO$	625.1	625.0
$(C_6F_5)_2SnFe(CO)_2cp^+ \rightarrow (C_6F_5)_2SnFecp^+ + 2CO$	524.0	524.0
$Ph(C_6F_5)\ SnFe(CO)_2cp^{+\cdot} \rightarrow Ph(C_6F_5)SnFecp^+ + 2CO$	434.8	435.0

In the spectrum of the silicon derivative, ions due to the loss of H, H_2 and F from the base peak $Ph(C_6F_5)_2SiFecp^{+\cdot}$ were observed, although only the loss of a fluorine radical was supported by the appropriate metastable transition,

	m* calc.	m* found
$Ph(C_6F_5)_2SiFecp \rightarrow Ph(C_6F_5)(C_6F_4)SiFecp + F$	522.6	523.0

The formation of the fluorocarbon fragments in this spectrum

Table 4-7

The 70 e.v. Mass Spectra of the Compounds $Ph(C_6F_5)_2MMn(CO)_5$

Ion M =	Relative Abundance % Si	Ge	Sn
a) Ions containing two metals:			
$Ph(C_6F_5)_2MMn(CO)_5^{+\cdot}$	0.4	1.0	4.1
$Ph(C_6F_5)_2MMn(CO)_4^{+\cdot}$	3.5	2.2	1.3
$Ph(C_6F_5)_2MMn(CO)_3^{+\cdot}$	0.1		
$Ph(C_6F_5)_2MMn(CO)_2^{+\cdot}$	1.1		
$Ph(C_6F_5)_2MMnCO^{+\cdot}$	0.5		
$Ph(C_6F_5)_2MMn^{+\cdot}$	10.6	6.2	2.9
$Ph(C_6F_5)MMn(CO)_5^{+}$		0.2	0.3
$F_3MMn^{+\cdot}$			0.7
b) Ions containing one metal:			
$Ph(C_6F_5)_2MF^{+\cdot}$ a)	0.4		
$Ph(C_6F_5)_2M^{+}$	10.6	8.2	10.6
$C_{18}F_9H_4M^{+\cdot}$		0.2	0.3
$C_{18}H_5F_8M^{+}$	0.2		
$C_{18}F_8H_4M^{+\cdot}$	0.7		
$Ph(C_6F_5)MF^{+}$		0.9	0.8
$(C_6F_5)_2MF^{+}$	1.1		
$C_6F_5M^{+}$	b)	0.3	1.8
$PhMF_2^{+}$	1.2		
PhM^{+}	4.4	43.0	29.9
$C_4H_3M^{+}$	c)	1.0	0.7

a) Ion formed by ion-molecule reaction
b) overlapped by $Mn(CO)_5^{+}$
c) overlapped by $C_5F^{+\cdot}$

Table 4-7 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
MF^+	1.0	7.3	10.0
$M^{+\cdot}$		0.5	3.2
$Mn(CO)_5^+$	0.1	0.1	0.7
$Mn(CO)_4^+$ d)			
$Mn(CO)_3^+$	0.2	0.2	e)
$Mn(CO)_2^+$	0.3	0.3	0.4
$MnCO^+$	0.6	0.6	0.9
Mn^+	3.7	4.8	4.0
$(C_6F_4)_2Mn^+$	0.2		
$C_6F_5Mn^{+\cdot}$		0.1	0.4
$PhMn^{+\cdot}$	1.8	1.1	0.7
MnF_2^+	0.4	f)	0.3
$MnF^{+\cdot}$	2.4	2.0	1.5
c) Hydrocarbon/fluorocarbon Ions:			
$(C_6F_5)_2^{+\cdot}$	1.4		
$C_{12}F_9H^{+\cdot}$	3.3		
$C_{12}F_9^+$	0.7		
$C_{12}F_8^{+\cdot}$	2.8		
$C_{12}F_7H^{+\cdot}$	1.0		
$C_{12}F_7^+$	1.0		
$C_{12}F_3H_5^+$	2.1	0.6	
$C_{12}F_2H_5^{+\cdot}$	2.2	0.5	
$C_{12}F_2H_4^+$	1.2	0.6	

d) overlapped by $C_6F_5^+$
e) overlapped by $Sn^{120}F^+$
f) overlapped by $Ge^{73}F^+$

Table 4-7 cont'd

Ion M =	Relative Abundance % Si	Ge	Sn
$C_6F_4H^{+\cdot}$	1.1	g)	0.2
$C_6F_3^{+\cdot}$	0.7		
$C_6F_2^{+}$	0.4		
$C_5F_2^{+}$	0.5		
$C_5F^{+\cdot}$	0.5	0.2	0.3
$C_6F_5H^{+\cdot}$	2.1	0.7	2.1
$C_6F_5^{+}$	0.8	0.3	0.3
$C_6F_4^{+\cdot}$	0.3	0.4	0.2
$C_5F_2H^{+\cdot}$	1.3	0.6	1.1
$C_6H_6^{+\cdot}$	0.5	0.3	0.7
Ph^{+}	2.6	2.2	3.5
$C_4H_3^{+}$	1.7	1.4	2.0
$C_4H_2^{+\cdot}$	0.4	0.4	0.4

g) overlapped by $PhGe^{72+}$

Partial Fragmentation Pattern for $Ph(C_6F_5)_2SiMn(CO)_5$

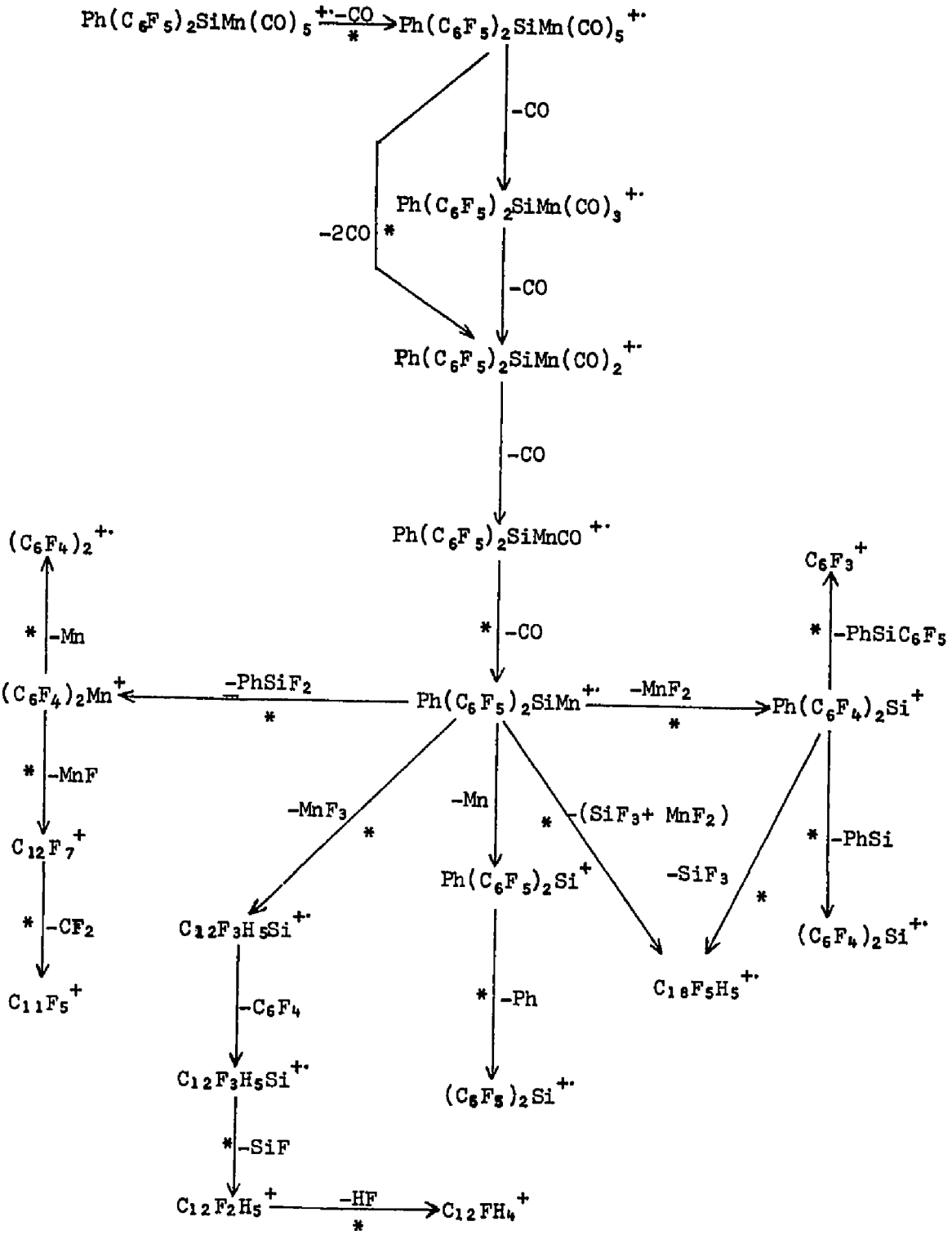


Figure 4-19

Partial Fragmentation Pattern for $Ph(C_6F_5)_2GeMn(CO)_5$

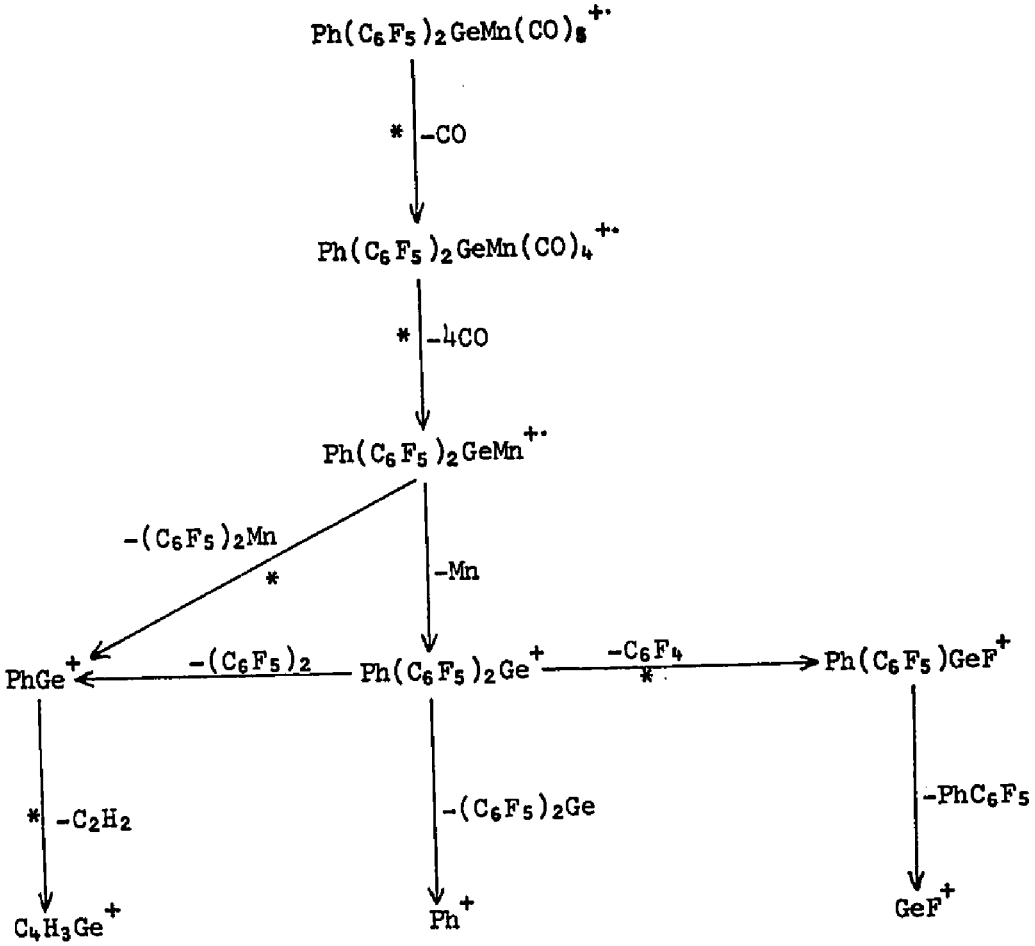


Figure 4-20

Partial Fragmentation Pattern for $Ph(C_6F_5)_2SnMn(CO)_5$

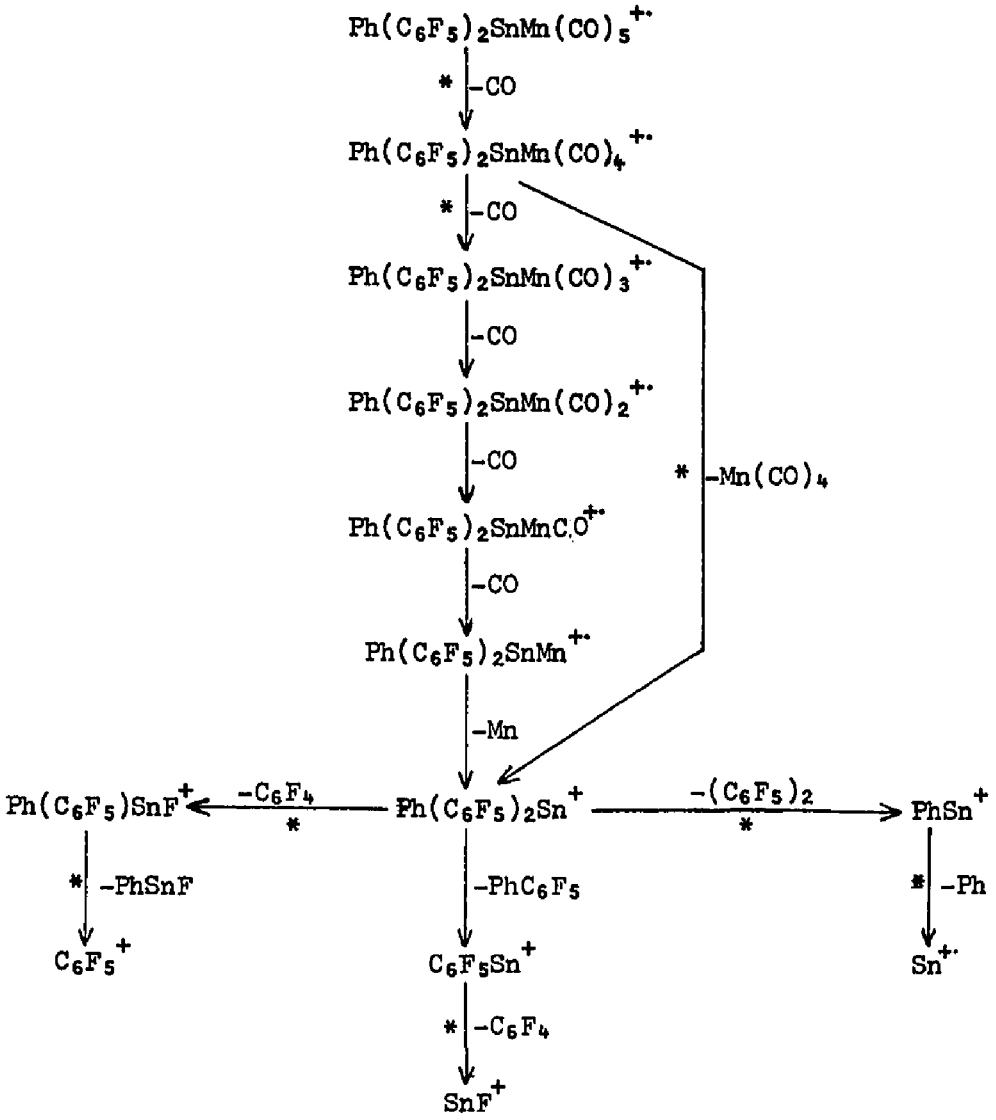


Figure 4-21

would be expected to arise by the loss of a silicon and iron fluoride species from the ion $Ph(C_6F_5)_2SiFecp^+$, but although none of these were observed, this compound did show the comparatively rare metastable transition,

	m* calc.	m* found
$Ph(C_6F_5)_2SiFe(CO)cp^{+\cdot} \rightarrow (C_6F_4)_2^{+\cdot} + PhSiF_2 +$ Fe(CO) cp	149.1	149.0

The ions $FFecp^{+\cdot}$ and $Fecp^+$ were fairly abundant and the formation of $Fecp^+$ was supported by the metastable transition

	m* calc.	m* found
$Ph(C_6F_5)_2SiFecp^{+\cdot} \rightarrow Fecp^+ + Ph(C_6F_5)_2Si$	26.1	26.0

by contrast, the alternative framentation to give the ion $Ph(C_6F_5)_2Si^+$ does not occur to any great extent, and is in keeping with the low abundances of the $Ph(C_6F_5)_2M^+$ and $(C_6F_5)_3M^+$ ions found in the mass spectra of the other bis(pentafluorophenyl) and tris(pentafluorophenyl) derivatives.

The ion $PhSiF_2^+$, presumably formed by the loss of $(C_6F_4)_2$ from the $Ph(C_6F_5)_2Si^+$ ion, was observed to eliminate SiF_2, while the ions

	m* calc.	m* found
$PhSiF_2^+ \rightarrow Ph^+ + SiF_2$	41.5	41.5

$Fecp^+$ and $FFecp^{+\cdot}$ were observed to fragment as described previously for the derivatives $Ph_3GeFe(CO)_2cp$ and $(C_6F_5)_3SiFe(CO)_2cp$ respectively.

	m* calc.	m* found
$FFecp^{+\cdot} \rightarrow C_5H_4Fe^{+\cdot} + HF$	102.9	102.8
$FFecp^{+\cdot} \rightarrow FeF^+ + cp$	40.2	40.2

	m* calc.	m* found
$Fecp^+ \rightarrow Fe^{+\cdot} + cp$	34.9	34.9
$Fecp^+ \rightarrow C_3H_3Fe^+ + C_2H_2$	74.6	74.5

In the spectrum of the tin derivative, only the ions $PhFecp^+$, $PhSn^+$ and SnF^+ have large abundances; in contrast to the spectrum of $Ph_2(C_6F_5)SnFe(CO)_2cp$ where in addition to these ions, there are also large abundances of the ions $Ph_2(C_6F_5)SnFe(CO)_ncp^+$ (n = 0 to 2), $Ph_2(C_6F_5)Sn^+$, and $Ph(C_6F_5)SnFecp^+$. However, despite the small intensities of many of these ions a large number of metastable transitions were seen and follow the same fragmentation routes as those previously found for the other phenyl(pentafluorophenyl) tin species. Thus the $Ph(C_6F_5)_2Sn^+$ ion was observed to lose C_6F_4, followed by PhF, and finally C_6F_4 again to form the SnF^+ ion,

	m* calc.	m* found
$Ph(C_6F_5)_2Sn^+ \rightarrow Ph(C_6F_5)SnF^+ + C_6F_4$	215.1	215.0
$Ph(C_6F_5)SnF^+ \rightarrow C_6F_5Sn^+ + PhF$	215.1	215.0
$C_6F_5Sn^+ \rightarrow SnF^+ + C_6F_4$	67.3	67.5

while the tin ion was shown to be formed by the loss of phenyl from $PhSn^+$, or cp from $cpSn^+$.

	m* calc.	m* found
$PhSn^+ \rightarrow Sn^{+\cdot} + Ph$	73.1	73.1
$Sncp^+ \rightarrow Sn^{+\cdot} + cp$	77.8	78.0

The ion $Ph(C_6F_5)_2SnFecp^{+\cdot}$ was shown to lose $(C_6F_5)_2Fe$ or $C_{12}F_9$,

	m* calc.	m* found
$Ph(C_6F_5)_2SnFecp^{+\cdot} \rightarrow PhSncp^{+\cdot} + (C_6F_5)_2Fe$	105.5	105.5
$Ph(C_6F_5)_2SnFecp^{+\cdot} \rightarrow Ph(F)SnFecp^+ + C_{12}F_9$	174.2	174.1

and in an analogous manner to the fragmentation of the $(C_6F_5)_3SnFecp^+$ ion, was also observed to lose C_6F_5 or $(C_6F_5)_2Sn$.

	m* calc.	m* found
$Ph(C_6F_5)_2SnFecp^{+\cdot} \rightarrow Ph(C_6F_5)SnFecp^+ + C_6F_5$	360.8	361.0
$Ph(C_6F_5)_2SnFecp^{+\cdot} \rightarrow PhFecp^+ + (C_6F_5)_2Sn$	60.1	60.0

The latter process seems to dominate the fragmentation.

The base peak $PhFecp^+$ was shown to undergo the characteristic loss of hydrogen or acetylene,

	m* calc.	m* found
$PhFecp^{+\cdot} \rightarrow C_{11}H_8Fe^{+\cdot} + H_2$	194.0	194.0
$PhFecp^{+\cdot} \rightarrow C_9H_8Fe^+ + C_2H_2$	149.4	149.4

while the ion $PhSnCp^{+\cdot}$ was also shown to be formed by the loss of C_6F_5Fe from the ion $Ph(C_6F_5)SnFecp^+$.

	m* calc.	m* found
$Ph(C_6F_5)SnFecp^+ \rightarrow PhSncp^{+\cdot} + C_6F_5Fe$	234.1	234.0

Finally the rearrangement ion $PhFe(CO)_2cp^+$, presumably formed by the loss of $(C_6F_5)_2Sn$ from the molecular ion, or by the loss of C_6F_5Sn from the ion $Ph(C_6F_5)SnFe(CO)_2cp^+$, was shown to lose CO or phenyl and finally the cyclopentadienyl radical to form the ion $Fe^{+\cdot}$.

	m* calc.	m* found
$PhFe(CO)_2cp^{+\cdot} \rightarrow PhFe(CO)cp^{+\cdot} + CO$	125.4	125.5
$PhFe(CO)cp^{+\cdot} \rightarrow PhFecp^{+\cdot} + CO$	98.2	98.2
$PhFe(CO)cp^{+\cdot} \rightarrow Fecp^+ + Ph$	173.5	173.5
$Fe(CO)cp^+ \rightarrow Fecp^+ + CO$	98.2	98.2
$Fecp^+ \rightarrow Fe^{+\cdot} + cp$	25.9	25.9

Table 4-8

The 70 e.v. Mass Spectra of the Compounds $Ph(C_6F_5)_2MFe(CO)_2cp$ (M = Si or Sn)

Ion M =	Relative Abundance % Si	Sn
a) Ions containing two metals		
$Ph(C_6F_5)_2MFe(CO)_2cp^{+\cdot}$	0.1	1.7
$Ph(C_6F_5)_2MFe(CO)cp^{+\cdot}$	1.9	1.3
$Ph(C_6F_5)_2MFecp^{+\cdot}$	15.1	3.0
$Ph(C_6F_5)MFe(CO)_2cp^{+}$		1.7
$Ph(C_6F_5)MFecp^{+}$	0.2	1.5
$(C_6F_5)_2SnFe(CO)_2cp^{+}$		<0.1
$(C_6F_5)_2SnFecp^{+}$		<0.1
$C_{23}H_9F_{10}MFe^{+}$	2.6	
$C_{23}H_{11}F_9MFe^{+\cdot}$ a	1.1	
$C_{23}H_9F_9MFe^{+\cdot}$	1.1	
$C_{23}H_8F_9MFe^{+}$	0.5	
$PhM(F)Fecp^{+}$		0.1
$M\text{-}Fe^{+\cdot}$		0.1
b) Ions containing one metal		
$Ph(C_6F_5)_2M^{+}$	0.1	1.2
$Ph(C_6F_5)MF^{+}$	0.1	0.8
$C_6F_5M^{+}$	0.1	0.7
$C_{18}H_5F_8M^{+}$	0.2	
$C_{18}H_4F_8M^{+\cdot}$	0.2	
$C_{18}H_3F_8M^{+}$	0.9	
$PhMcp^{+}$	0.1	0.1

a) Ion formed by ion-molecule reaction

Table 4-8 cont'd.

Ion M =	Relative Abundance % Si	Sn
$C_{11}H_9M^{+\cdot}$		1.7
PhM^+	0.9	6.2
cpM^+	0.2	3.1
$C_4H_3M^+$	0.3	
MF^+	1.1	7.1
$M^{+\cdot}$		2.1
$C_{23}H_7F_{10}Fe^+$	0.1	
$C_{23}H_6F_{10}Fe^{+\cdot}$	0.2	
$(C_6H_4)(C_6F_4)Fecp^+$		0.1
$PhFe(CO)_2cp^{+\cdot}$		0.1
$PhFe(CO)cp^{+\cdot}$		0.2
$PhFecp^{+\cdot}$	0.1	24.5
$C_{11}H_8Fe^+$		1.2
$C_9H_8Fe^{+\cdot}$		0.5
$FFecp^{+\cdot}$	5.4	0.6
$Fe(CO)_2cp^+$	0.2	0.5
$Fe(CO)cp^+$	0.7	1.1
$Fecp^+$	6.7	3.2
$C_3H_3Fe^+$	0.7	2.0
$FeF_2^{+\cdot}$	0.5	
FeF^+	1.4	0.2
$Fe^{+\cdot}$	5.2	2.1

Table 4-8 cont'd

Ion M =	Relative Abundance % Si	Sn
c) Hydrocarbon/Fluorocarbon Ions		
$C_{18}F_5H_5^{+\cdot}$	0.9	
$C_{17}F_3H_5^{+\cdot}$	1.1	
$C_{17}F_2H_5^{+}$	0.5	
$C_{12}F_3H_5^{+\cdot}$	1.8	
$C_{12}F_2H_4^{+\cdot}$	0.9	
$C_{11}H_5F_2^{+}$	0.5	
$(C_6F_5)_2^{+\cdot}$	0.6	
$(C_6F_4)_2^{+\cdot}$	0.7	
$C_6F_6^{+\cdot}$	0.3	0.3
$C_6F_5H^{+\cdot}$	1.0	2.1
$C_6F_5^{+}$	0.5	
$Phcp^{+\cdot}$	0.2	2.1
$C_{11}H_8^{+}$		0.8
$C_5F_2H^{+}$	0.5	0.6
$PhH^{+\cdot}$	0.2	0.8
Ph^{+}	3.0	4.7
C_5F^{+}	b	0.5
$cpH^{+\cdot}$	0.7	0.6
cp^{+}	0.9	0.5
$C_4H_3^{+}$	0.3	1.4
$C_4H_2^{+\cdot}$		0.2

b) Masked by $C_4H_3Si^{+}$

Partial Fragmentation Pattern for $Ph(C_6F_5)_2SiFe(CO)_2cp$

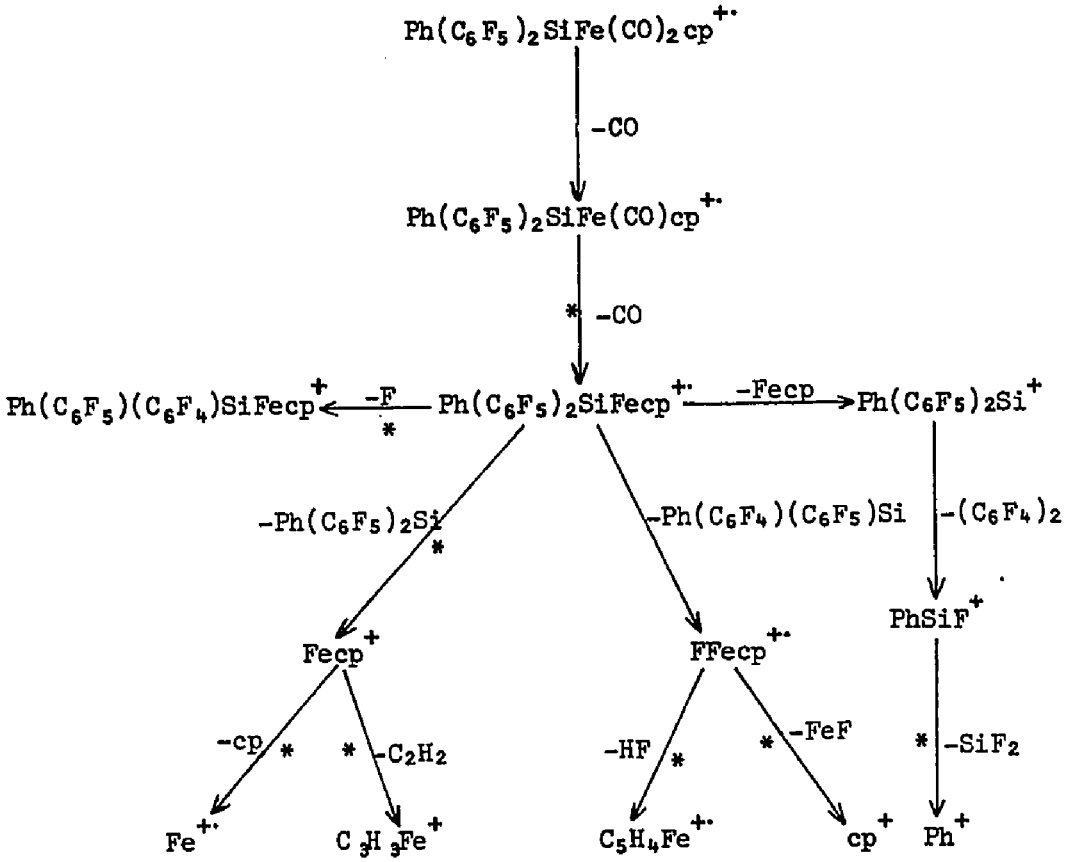


Figure 4-22

Partial Fragmentation Pattern for $Ph(C_6F_5)_2SnFe(CO)_2cp$

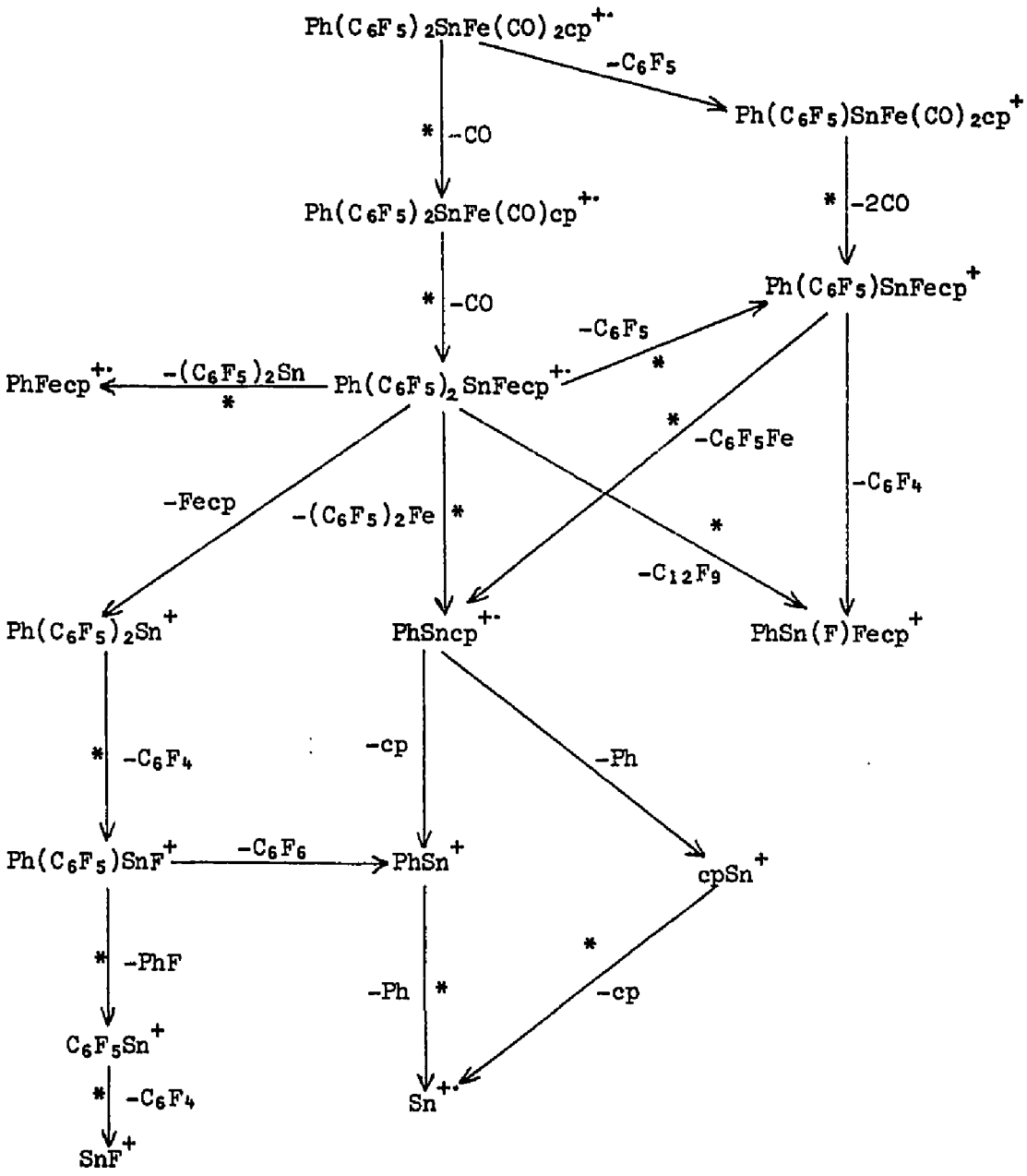


Figure 4-23

11) Modes of Fragmentation

In order to facilitate the comparison between the modes of fragmentation, the abundance of each ion type as a percentage of the total positive ion current is given in Table 4-9 for the compounds Ph_3MX and $(C_6F_5)_3MX$ (X = $Mn(CO)_5$ or $Fe(CO)_2cp$), while those for the derivatives $Ph_2(C_6F_5)MX$ and $Ph(C_6F_5)_2MX$ are shown in Table 4-10.

In all these spectra, most of the ion current is carried by the metal containing ions, but the abundances of these tend to decrease as phenyl is successively replaced by C_6F_5, such that the spectra of the fluorocarbon derivatives tend to show a higher abundance of fluorocarbon and hydrocarbon ions. The most common mode of fragmentation is the loss of an odd-electron fragment from an odd electron ion, or an even electron fragment from an even electron ion such that even electron ions dominate the spectra; although in some cases, odd electron ions other than those formed by loss of carbonyl, and particularly those that are formed by rearrangement process can be quite abundant e.g. $Ph_3Mn^{+\cdot}$, $PhFecp^{+\cdot}$.

A comparison of the ion types in the mass spectra of the Ph_3MX derivatives show that except for the lead derivatives the abundances of the ions containing two metals, and hence the rearrangement ions from which they come, are higher for the derivatives where X = $Fe(CO)_2cp$ than for those where X = $Mn(CO)_5$. This is however not an indication of the difference in the relative metal-metal bond strength between the two series, although in some other compounds containing metal-metal bonds, the trend in the abundances of the ions containing two metals do bear a rather remarkable but certainly fortuitous

relationship to the trend in bond strengths derived from appearance potential data (40, 41). This observation is rather surprising since there is no real reason why these odd electron ions, particularly those containing a Si-Fe or Ge-Fe bond, should be more stable than the analogous Group IV-manganese ions, but it is worth noting that for the other compounds in this work, the ions containing a metal-iron bond generally have larger abundances than do those containing a metal-manganese bond.

The change in the fragmentation mode involving the cleavage of the carbon-carbon bond in the phenyl ring, seen to be almost exclusive for the silicon derivative, to that involving the cleavage of the phenyl metal-bond which predominates for the tin and lead derivatives, is responsible for the larger abundances of the hydrocarbon and rearrangement ions observed for these heavier elements. Similar effects have also been noted for some other metal-metal bonded derivatives of the type $R_3M\text{-}M'_3R'$ (R and R′ = alkyl or aryl M = M′ = a Group IV metal) (198).

For the tris(pentafluorophenyl) derivatives while there is no apparent trend in the abundances of the ions containing a metal-metal bond, the abundances of the ions formed by the migration of a fluorine atom and of the rearrangement ions, increase as the Group IV metal becomes heavier, and consequently give higher abundances for the hydrocarbon or fluorocarbon ions. As for the Ph_3MX derivatives the formation of a rearrangement ion is more favoured where X = $Fe(CO)_2cp$, and thus decreases the abundances of the ions containing one metal, but increases the abundances of the

hydrocarbon and fluorocarbon ions relative to those where X = $Mn(CO)_5$.

In the series $Ph_2(C_6F_5)MX$ and $Ph(C_6F_5)_2MX$, while the abundances of the ion type show essentially the same trends for X = $Mn(CO)_5$, there is a more distinct contrast between the spectra of the silicon and tin derivatives where X = $Fe(CO)_2cp$. For the silicon derivatives, processes leading to the formation of a rearrangement ion are not important, since the major fragmentation route is the formation of a metal fluoride species, and is once again more favoured when X = $Fe(CO)_2cp$. For the tin derivatives the abundances of the metal-fluoride ions are less than for the silicon derivatives, but the abundances of the rearrangement ions are very much greater. This suggests that fragmentation by the loss of a C_6F_4 species to give a metal fluoride ion, which is the more dominant mode in the case of $(C_6F_5)_3SnFe(CO)_2cp$, is now of lesser importance than the formation of a rearrangement ion, particularly those containing phenyl. This is very evident in the mass spectra of $Ph(C_6F_5)_2SnFe(CO)_2cp$.

12) Measurement of the Bond Association Energies in $Ph_3SnMn(CO)_5$ and $Ph_3SnFe(CO)_2cp$

In spite of the fact that some indication of the absolute or relative bond strength of the metal-metal bond is essential to the understanding of the nature of the metal-metal bond there have only been a few attempts to measure these bond strengths by mass spectrometry (36 - 45). Even though some formidable experimental difficulties are often encountered, the real problem for organometallic compounds is the lack of the necessary thermochemical or ionisation potential data needed to effect such calculations. Where these have been reported

Table 4-9

Abundances for each Ion Type Expressed as a Percentage of the total Positive Ion Current for the Compounds Ph_3MX and $(C_6F_5)_3MX$

X = $Mn(CO)_5$ (a) or $Fe(CO)_2cp$ (b)

i) Ph_3MX

Ion type	M = Si		Ge		Sn		Pb	
	a)	b)	a)	b)	a)	b)	a)	b)
Ions containing two metals	3	31	3	21	12	24	4	5
Ions containing one metal	93	66	92	68	77	59	57	63
Rearrangement ions	1	0	2	6	2	11	24	14
Hydrocarbon ions	3	3	3	4	8	6	15	18

ii) $(C_6F_5)_3MX$

Ion type	M = Si		Ge		Sn	
	a)	b)	a)	b)	a)	b)
Ions containing two metals	32	20	23	26	18	16
Ions containing one metal[a]	20	24	40	17	34	20
Metal Fluoride ions[b]	13	17	23	18	30	26
Rearrangement ions[c]	2	4	1	12	2	16
Hydrocarbon/Fluorocarbon ions	33	35	13	27	6	22

a) does not include metal fluoride or rearrangement ions
b) does not include metal-metal fluoride ions
c) does not include metal fluoride ions

Table 4-10

Abundances for Each Ion Type Expressed as a Percentage of the Total Positive Ion Current for the Compounds $Ph_2(C_6F_5)MX$ and $Ph(C_6F_5)_2MX$ X = $Mn(CO)_5$ (a) or $Fe(CO)_2cp$ (b)

i) $Ph_2(C_6F_5)MX$

Ion type	M = Si		Ge		Sn	
	a)	b)	a)	b)	a)	b)
Ions containing two metals	22	29	11		11	24
Ions containing one metal[a]	28	27	66		60	38
Metal Fluoride ions[b]	9	26	12		15	10
Rearrangement ions[c]	2	0	1		1	18
Hydrocarbon/Fluorocarbon ions	39	18	9		13	10

ii) $Ph(C_6F_5)_2MX$

Ion type	M = Si		Ge		Sn	
	a)	b)	a)	b)	a)	b)
Ions containing two metals	19	37	22		19	11
Ions containing one metal[a]	54	26	54		61	25
Metal fluoride ions[b]	7	14	15		9	11
Rearrangement ions[c]	1	1	1		1	36
Hydrocarbon/Fluorocarbon ions	19	22	8		10	17

a) does not include metal fluoride or rearrangement ions
b) does not include metal-metal fluoride ions
c) does not include rearrangement ions

their true value is often incertain since, depending on the operating conditions of the various instruments, and the procedure used in determining the appearance potential, a notoriously large variance in the ionisation potential for a given species can result (169).

The measurement of the metal-metal bond strength in the binuclear metal carbonyls $M_2(CO)_{10}$ (M = Mn, and/or Re) (42, 43), $Co_2(CO)_8$ (42), $[M(CO)_3cp]_2$ (M = Mo or W) (39), $[M(CO)_2cp]_2$ (M = Fe or Ru) (39), and in compounds of the type $Me_3MM'Me_3$ (169) (M M' = Group IV metal) has been reported, but the number of studies on a Group IV-transition metal bond are relatively few and are shown in Table 4-11.

In these studies the assumption is made that in the dissociation

$$R_3MX^{+\cdot} \rightarrow R_3M^+ + X$$

(R = alkyl, aryl or halide, M = a Group IV metal and X = a transition metal carbonyl)

there is no excitational or excess kinetic energy involved in the breaking of the M-X bond so that the bond dissociation energy D(M-X) is given by

$$D(M-X) = AP(R_3M^+) - IP(R_3M)$$

In the compounds under study here, the bond dissociation energy of the tin manganese or tin iron bond may thus be calculated if the ionisation potential of the Ph_3Sn radical is known. The value reported by Glockling et al of 6.0±0.4 e.v. (201) appears to be too low since it is reasonable to expect that its true value should be about the same as that for Me_3Sn at 6.77 e.v. (40, 44, 169, 202), and thus on this basis the more recent value of 6.9±0.1 e.v. (203) appears to be more reliable. In this work the error weighted value

between these two results of 6.85±0.1 e.v. was used.

The effect of any excitational energy in the dissociation of the metal-metal bond cannot be estimated but is assumed to be very low, and according to Stevenson's rule (204), if in the dissociation

$$A\text{-}B^{+} \rightarrow A^{+} + B$$

the ionisation potential of B is greater than that of A, then it can be assumed that there is no excess kinetic energy involved in the reaction. This is also true in the present case since the ionisation potentials of both $Mn(CO)_5$ (8.44±0.1 e.v.) (42) and $Fe(CO)_2cp$ (7.70±0.10 e.v.) (39) are both greater than the ionisation potential of the Ph_3Sn radical.

However, there may be other processes that lead to formation of the Ph_3Sn^{+} ion, than just by the elimination of the transition metal carbonyl radical. These processes will have different energies and thus affect the appearance potential of the ion under investigation. The mass spectra of the compounds under study here show that although the metastable-supported-loss of $Mn(CO)_5$ or $Fe(CO)_2cp$ from the molecular ion was observed in both cases, the loss of one or more carbonyl groups and then manganese or Fecp could also be processes leading to the formation of the Ph_3Sn ion. However, this is not very likely since the ionic bond dissociation energies for the loss of one carbonyl group in the very comparable systems, $Me_3SiMn(CO)_5$ (44) and $Me_3GeMo(CO)_2cp$ (41) are of the same order of magnitude as that of the metal-metal bond. Thus the loss of more than one carbonyl group would be expected to have a higher bond dissociation energy than that needed to cleave the metal-metal bond, and so cannot be

considered to contribute substantially to the formation of the Me_3M ion, at least in the threshold region where the appearance potential measurements are made. It is also possible that the Ph_3Sn ion could arise from thermal pyrolysis of the sample within the ion source, but again this is rather unlikely since the temperatures of the probe and ion source were not enough to even melt the sample. It has also been shown that for the compounds $Me_3MM'(CO)_3Cp$ (M = Ge or Sn and M' = Cr, Mo, or W) there is, within experimental error, no change in the appearance potential of the Me_3M^+ ion over a temperature range of 100 - 150° (41), which is higher than that used in this study. In addition, a thermal pyrolysis study of $Me_3SnMn(CO)_5$ (44) shows that this compound only begins to decompose above a source temperature of 300°, and in view of the similar thermal stability of this compound with the ones under study here, it does not seem likely that any extensive thermal decomposition takes place.

Further evidence that there is only one process leading to the formation of the Ph_3Sn^+ ion can also be obtained from the shape of the ionisation efficiency curve, since, according to Morrison (205), ions that exhibit long tails in their ionisation efficiency curves probably arise from two or more processes. Although it does not provide conclusive evidence, the ionisation efficiency curves for the Ph_3Sn^+ ion obtained in this work are nearly parallel to that for the xenon standard for which only one process is possible, and thus provides good evidence against the formation of the Ph_3Sn^+ ion by more than one process.

From the measured appearance potential of the Ph_3Sn ion produced

from $Ph_3SnMn(CO)_5$ (9.50±0.14 e.v.) and from $Ph_3SnFe(CO)_2cp$ (9.16±0.29 e.v.) the bond dissociation energies of the Sn-Mn and Sn-Fe bonds were calculated to be 61±8 Kcals/mole and 54±9 Kcals/mole respectively. These values are of a similar magnitude to those found for $Me_3MMn(CO)_5$ (44) (Table 4-11) but as for the latter compounds, the errors are enough to hide any real trend if this is present at all. However, the observed increase in strength for the Sn-Mn bond is in keeping with its greater resistance to attack by halogens, [Chapter 2(3)], but not with the decreased p donor properties of the $Mn(CO)_5$ group as determined by the Mossbauer spectra. The variation in the metal-metal bond strengths for the series $Me_3MM'(CO)_3cp$ (M = Ge or Sn and M' = Cr, Mo or W) (41) has been defended on the grounds of steric effects and the thermal stability of the Me_3M and $M'(CO)_3cp$ radicals, but since an error of at least ±15% can be expected by this method it is doubtful whether there is any justifiable difference in the bond strength between the tin or germanium compounds, although there does appear to be an increase in the metal-metal bond strength when M' = Mo or W over that for M' = Cr.

The unusually high silicon-metal strengths in the compounds $RCo(CO)_4$ (R = F_3Si, MeF_2Si and Cl_3Si) (190) have been taken as an indication of a strong silicon-cobalt bond, but even allowing for the uncertainty in the value for the heat of formation of the $Co(CO)_4$ radical, which could lower the value of the silicon bond strength by 31 Kcals/mole, these values are not in agreement with the observations from vibrational (206) and other mass spectrometric studies (169) that the silicon-metal bond energy is about the same

as that for a tin-metal bond,or if anything is possibly weaker. A possible explanation for these high bond strengths lies in the fact that the R^+ ion is not produced from the silicon-cobalt compound but from the products of the thermal pyrolysis of the sample.

The compound $F_3SiCo(CO)_4$ is known not to be very stable above room temperature (207), and thus even in a warm ion source could decompose to give SiF_4, CoF_2 and CO. Analogous decompositions probably occur in the other silicon cobalt derivatives, and it is worth noting that the mass spectra of $Cl_2GaMn(CO)_5$ also shows extensive decomposition to give peaks due to $GaCl_3^+$ (208). Thus the measured bond strength may not be of the silicon-cobalt bond but of the silicon-fluoride bond and is in keeping with the accepted values for the high bond strength of the main group fluorides (209).

In conclusion, it would appear that this method of determining bond strengths is rather limited in its scope since, unless there is very good evidence that there are very substantial differences in the bond strength between a series or group of compounds, the values obtained are not particularly meaningful if they are to be used to correlate data collected via other methods, or used to explain differences in the chemical reactivity.

Table 4-11

The Bond Dissociation Energies for Some Group IV Transition Metal Bonds

Compound	D(M-M) Kcals/mole	Reference
$F_3SiCo(CO)_4$	105±12[a], 74	190
$MeF_2SiCo(CO)_4$	105±15[a], 96	190
$Cl_3SiCo(CO)_4$	95±25	190
$Me_3SiMn(CO)_5$	57±7	44
$Me_3GeMn(CO)_5$	62.5±8	44
$Me_3SnMn(CO)_5$	55±7	44
$Me_3PbMn(CO)_5$	47±12	44
$Me_3GeCr(CO)_3cp$	47[b]	41
$Me_3GeMo(CO)_3cp$	60	41
$Me_3GeW(CO)_3cp$	65	41
$Me_3SnCr(CO)_3cp$	53.5	41
$Me_3SnMo(CO)_3cp$	71	41
$Me_3SnW(CO)_3cp$	76	41
$Ph_3SnFe(CO)_2cp$	53±9	this work
$Ph_3SnMn(CO)_5$	61±8	this work

a) calculated using a high value for $\Delta H_f^\circ Co(CO)_4$
b) no error given

CHAPTER 5

INFRARED, RAMAN AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

1) Infrared Spectra in the Carbonyl Stretching Region

Studies in this area have been used to a) determine the symmetry of the transition metal carbonyl species and b) from this, to correlate the force constants derived from the carbonyl stretching frequency with the bonding parameters of the ligands.

The infrared spectra of metal carbonyl species in the region 1850 - 2150 cm^{-1} will give rise to several bands due to carbonyl stretching vibrations; the number and intensity of which will depend upon the particular point group to which the metal carbonyl belongs. Very often the structures that are assigned on the basis of infrared evidence agree with those determined by X-ray crystallographic studies, so that compounds exhibiting similar spectra to a compound of known structure may be also assumed to have that structure.

However, there are certain features of some spectra that can lead to a misleading assignment of the point symmetry of the transition metal carbonyl, these being particularly evident when the compound is not sufficiently soluble for solution spectra and the spectra must be taken in the solid state. Some compounds exhibit two bands that are accidentally degenerate and cannot be resolved or, in other cases, the intensity of an infrared active band could be unexpectedly weak and hence not

taken into consideration when the symmetry is assigned. Furthermore, although a spectrum may indicate one particular point group, this could also arise because of a severe distortion of another species of different symmetry, and it is this fact that generally precludes the unambiguous assignment of structures that are closely related by symmetry.

There can also be a change in structure according to the phase in which the spectra was taken, such that structures that are assigned on the basis of solution spectra need not necessarily be the same as those in the solid state. Interactions in a condensed phase may change the spectra, but while minimal interactions can only be expected in the gas phase, the limited volatility of most compounds makes this unattainable. Accordingly, most spectra are taken in a non-polar solvent which sould be kept constant when comparisons between spectra are to be made. Cyclohexane is particularly useful, since the low polarity and the large steric requirements of this solvent give the sharpest and best resolved spectra.

For compounds of the type $LMn(CO)_5$, the symmetry around manganese is C_{4v} and will give rise to a three band spectrum of symmetry species $2a_1$ and e. However when L is distorted or assymmetric, the symmetry of the manganese is reduced from C_{4v} and the nominally infrared inactive b_1 mode becomes active, and is often concurrent with the splitting of the doubly degenerate e mode. Thus, in compounds where L = Cl_3M (M = Si, Ge or Sn) the carbonyl spectra consists of three bands, but when L = Ph_3M the twisting of the phenyl rings results in an unsymmetrical relationship of the ligand with the planar carbonyl

groups and results in the appearance of a very weak b_1 mode which becomes more intense as L becomes less symmetric. Thus, for ligands containing two different substituents on the Group IV atom the b_1 mode is readily apparent, but while a concurrent splitting of the e mode should also be apparent, this is not as readily observed. However, the infrared spectra of $(C_6F_5)_3GeMn(CO)_5$ shown in Figure 5-1 shows a strong b_1 mode and a splitting of the doubly degenerate e mode. It appears that this latter affect is promoted by fluorocarbon groups, since various fluoroalkyl derivatives of manganese pentacarbonyl also show this effect, its magnitude appearing to depend upon the size of the substituent on the β carbon atom (210). A similar splitting of the e mode occurs in compounds of the type $R_2R'MCo(CO)_4$ (M = Ge or Sn; R' = Cl, Br, or I, and R = Me or Ph), but not in compounds of the type $R_3MCo(CO)_4$ (46). This is thought to be due to the assymmetry of the $R_2R'M$ group, and not to a difference in the position of substitution around the five coordinate cobalt atom. If the $R_2R'M$ group is axially substituted, the point symmetry of the cobalt atom is C_{3v}, and three bands would be expected, but if it is equatorially substituted the symmetry is now C_{2v} and a four band spectra would always result, regardless of the symmetry of the ligand L. This type of equatorial substitution has not been observed crystallographically (211), and since the e mode is degenerate with a more symmetric ligand, the splitting of the e mode is almost certainly due to the assymmetry of L.

In theory (212), the e and the low frequency a_1 modes should be distinctly resolved such that the a_1 band has half the intensity of

The Infrared Spectrum of $(C_6F_5)_3GeMn(CO)_5$ in the Carbonyl Stretching Region a) the total spectrum and b) the expanded portion of the low frequency band showing the splitting of the e mode

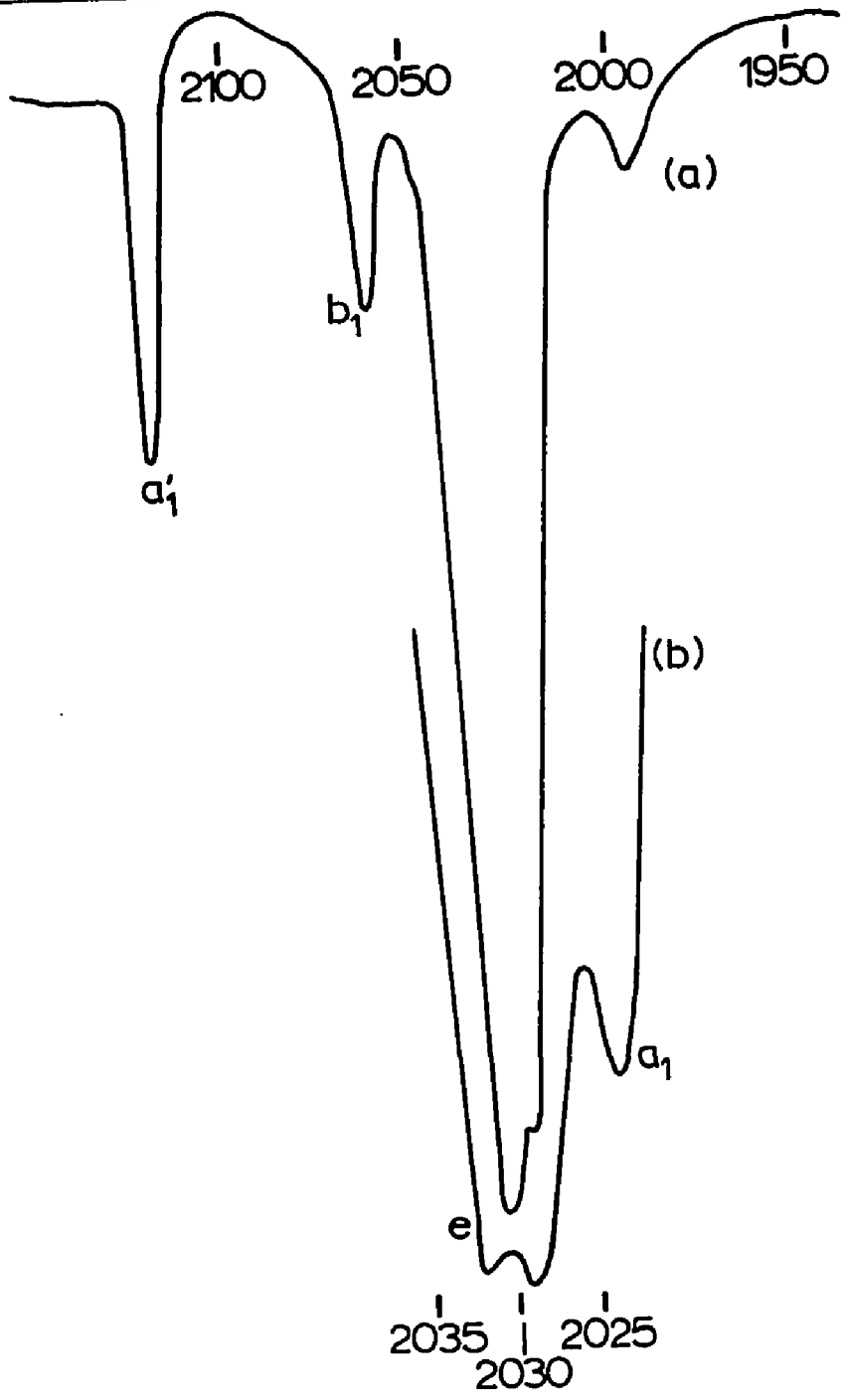


Figure 5-1

the e band. This effect is only evident in a few compounds, especially in derivatives of the type $Cl_3MMn(CO)_5$, where due to the high symmetry of the ligand Cl_3M, no b_1 mode is observed, and hence no splitting of the e band can be expected (48). For most of the compounds studied in this work however, the a_1 mode is of comparable intensity to the e mode, suggesting that although no splitting of the e mode was observed, some loss of symmetry had occurred. If this is the case, then the b nd width of the e mode should then be much larger than the a_1 mode and the assignments given in Table 5-1 are made on this basis. Similar arguments have been advanced to account for the band shape in $(C_6F_5)_3SnMn(CO)_5$ (52).

Some compounds, particularly those of the type $Ph_3MMn(CO)_5$, show no resolvable splitting presumably due to the accidental degeneracy of the a_1 and e modes which are thus assigned to the same frequency (48). In addition, the e mode can be at either a higher or lower frequency than the a_1 mode, and its relative position appears to be independent of the class or type of compound, such that its relative position cannot be readily predicted.

For species containing a $Fe(CO)_2cp$ group, the infrared spectra in the carbonyl stretching region show only two bands of equal intensity, and consistent with the C_{2v} symmetry of the carbonyl groups with respect to the iron atom.

Some molecules such as $Ph_3SnFe(CO)_2cp$ have been shown by X-ray crystallography (135) to contain two types of molecule in the unit cell, thus accounting for the four strong carbonyl stretching bands observed in the solid state spectra of this compound (51). However,

this does not seem to be a very general phenomenon since the solid state spectrum of $Cl_3SnFe(CO)_2cp$ (51) only shows two strong absorptions in the carbonyl stretching region, even though it has been shown that this compound also contains two distinct types of molecule per unit cell (135).

The solution infrared spectra of the series $RCl_2MFe(CO)_2cp$ (R = Ph or Me, and M = Si, Ge, or Sn) generally show that the two strong bands are split into unequal doublets, presumably due to different conformers in solution. This effect was first noted by Graham in the compound $MeCl_2MFe(CO)_2cp$ (M = Si or Sn) (69), for which the following conformers were proposed:

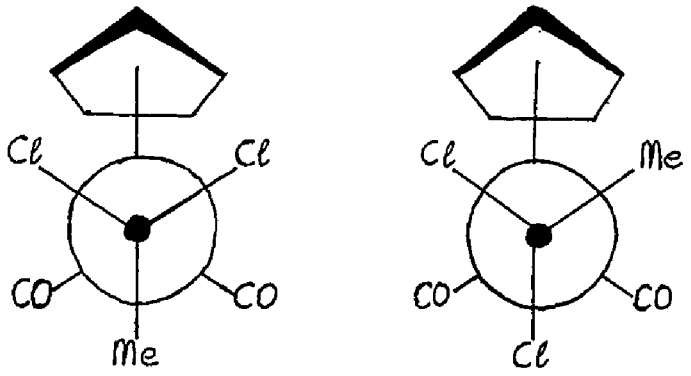


Figure 5-2

Possible Rotomers for $MeCl_2MFe(CO)_2cp$ (M = Si or Sn)

From further studies of the compound $MeCl_2SiFe(CO)_2cp$ (213) it was deduced that from enthalpy measurements, π-bonding in the SiFe bond can be considered to be unimportant, and that the appearance or the rotational isomers results from restricted rotation about the metal-metal bond due to steric effects alone.

Cullen et al noticed that this effect was present in

$Ph_3SnFe(CO)cpPPh_3$ (114), and ascribed this to a more general phenomenon that is not necessarily restricted to compounds where the ligands bonding to the Group IV atom are different.

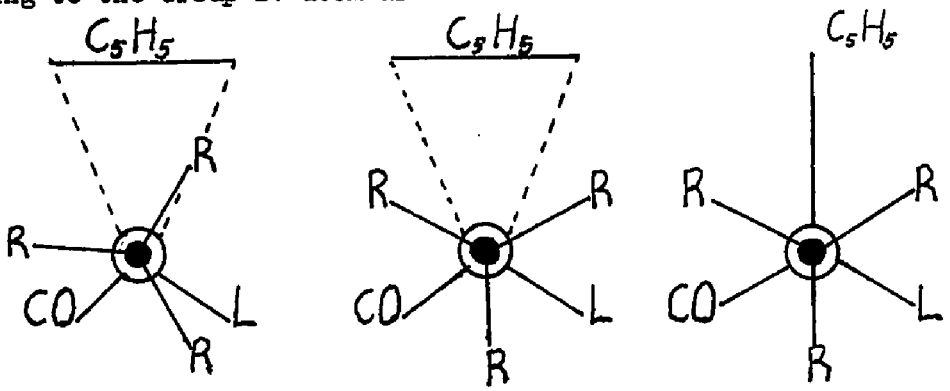


Figure 5-3

Possible Rotomers for $R_3SnFe(CO)cpL$

In the Figures 5-3 (a) and (b), the two structures differ because the R group bisects a different angle at the approximately octahedral coordinated iron atom, and gives rise to three rotomers having a fully staggered R group. In Figure 5-3 (c) the iron atom is tetrahedrally coordinated and only one completely staggered conformation is possible. It was suggested (114) that rotomers of the type (a) where present in solution and have sufficiently long life time to be detected by infrared spectroscopy, although compounds of similar structure, e.g. $Ph_3SnFe(CO)cpPPh_2CF_3$ which should exhibit similar splittings, failed to do so.

In the present work, compounds of the type $PhCl_2MFe(CO)_2cp$ (M = Si, Ge, or Sn) shown in Table 5-2 all showed some splitting of the carbonyl absorptions. However, the splitting was not particularly evident for the compounds $Ph(C_6F_5)_2MFe(CO)_2cp$ or $Ph_2XMFe(CO)_2cp$ (X = C_6F_5 or Cl), although quite often the bands exhibited shoulders

on either one or both peaks, suggesting that some sort of rotational conformers were present. The spectrum of $PhCl_2SiFe(CO)_2cp$ is shown in Figure 5-4. Compounds that were not very soluble in cyclohexane, such as $Ph_{3-n}X_nSnFe(CO)cpL$ (n = 1 to 3; L = CO, PEt_3 etc., X = Cl or Br) were run in chloroform as solvent, and with the exception of $Ph_3SnFe(CO)cpPPh_3$ showed no unusual features in their carbonyl spectra. It is known that more polar solvents interact with the electric dipole $C^{\delta+} = O^{\delta-}$ and increase its magnitude, thus decreasing the carbonyl frequency, and increasing the band width at half height (33). Thus the spectra taken in chloroform exhibited broader absorptions that those taken in cyclohexane, and this increase in band width could then mask any splitting of the bands.

The energies of the carbonyl stretching frequencies can be considered by three methods. The first of these is the theory of local oscillating dipoles (214, 215), which considers that the origin of the band at 2100 cm^{-1} is due to the totally symmetric stretching vibration. The position of this band is then related to the oxidation state (215), size of the substituent or the coplanarity of the transition metal with the equitorial carbonyl groups (214, 216).

The second type of correlation is by use of a correlation curve, in which the vibrational frequencies are plotted against the degree of substitution of a carbonyl compound by another ligand L. For a variety of ligands a family of curves results that converges upon a common point representing the frequency of the parent carbonyl. This type of approach has been used for the system $Me_3SnMn(CO)_{5-n}L_n$ (n = 0 to 2, L = phosphines, phosphites, etc), (16) and is particularly

The Infrared Spectrum of $PhCl_2SiFe(CO)_2cp$ in the Carbonyl Stretching Region

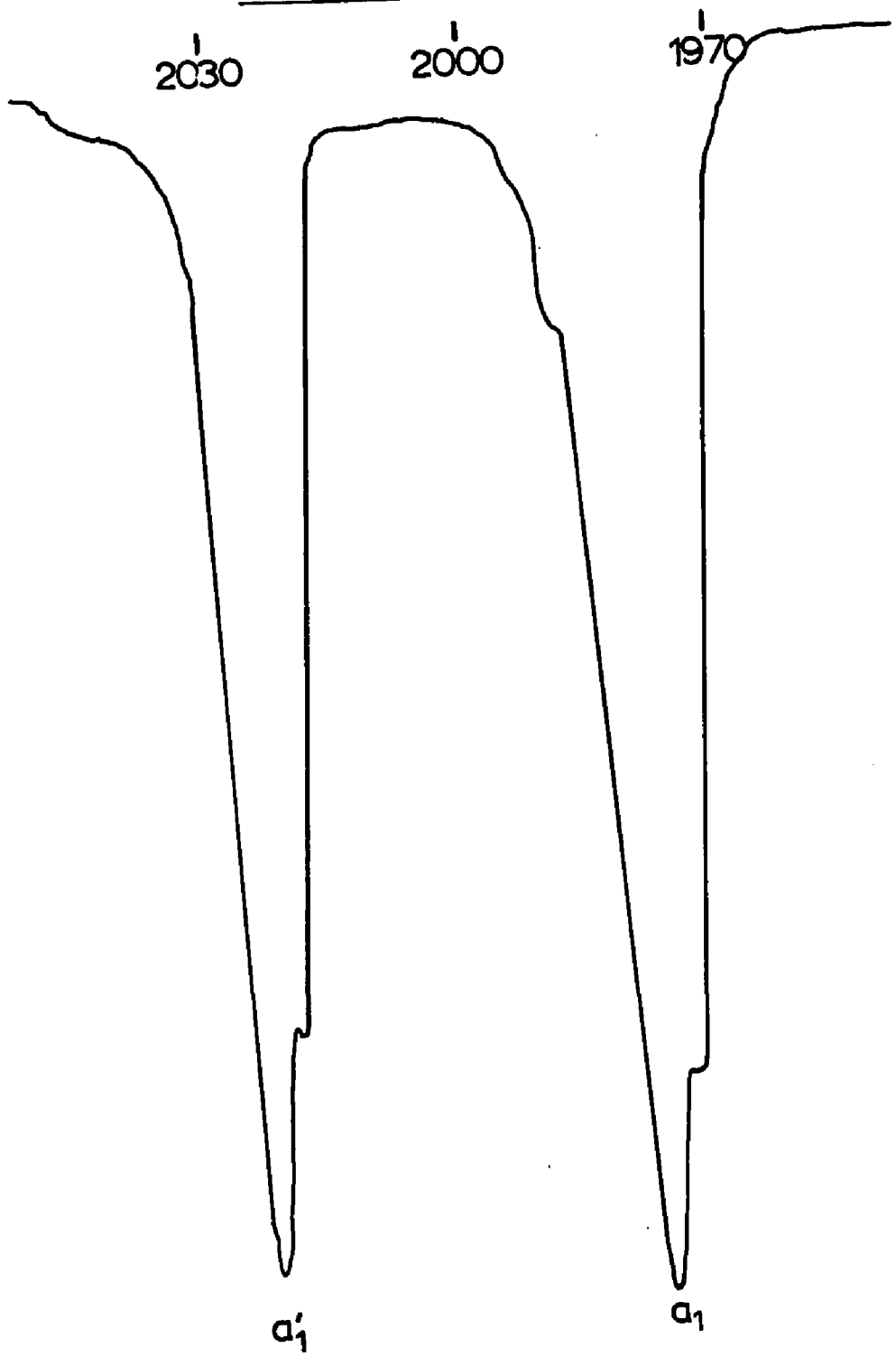


Figure 5-4

useful for determining the degree of substitution and structure for compounds that cannot be readily assigned from simple inspection of their infrared spectra.

By far the most widely used method is the Cotton-Kraihanzel (C.K.) approach (212), which neglects any anharmonic oscillations or coupling with other modes, and treats the CO stretching as an isolated harmonic dipole. In order to solve the secular equations, Cotton deduced that from elementary symmetry properties, the force constant (k_2) for the cis carbonyl must be greater than that for the trans(k_1), and that the carbonyl-carbonyl interaction force constant (k_i) must always be positive.

The simplest system is $LMn(CO)_5$ and the force constants can be calculated knowing only the positions of the a_1 and e modes. Normally only one assignment for all the possible bond symmetries is allowed if the values of k are such that the conditions $k_2>k_1$ and $k_i>0$ are to be satisfied.

Graham has calculated the C.K. force constants for a variety of metal-metal bonded compounds and has shown that the calculated frequencies of the b_1 mode are to within ± 3 cm^{-1} from those observed by infrared or Raman data (48). In a number of cases, the positions of the low frequency a_1 and e modes can be interchanged without seriously affecting the values of k_1 or k_2, but the assignments of these bands are usually made on the basis of either the relative intensities of the bands, or failing this, from an expected trend in k (48, 52).

Stone developed another approach, whereby k_2 is not assumed

to be related to k_1, but can only be used where all four carbonyl frequencies of the system $LMn(CO)_5$ are known. The force constants are allowed to vary over a fixed ratio and range, and the position of the highest frequency a_1 mode is calculated in each case. The values of k that give the closest value to the observed frequency are then taken as being correct (218, 219).

In order to use vibrational data as criteria for electronic structure it must be assumed that the CO stretching frequencies and hence the force constants are related to bond properties. If it is assumed that the charge on the metal resulting from the σ donor properties of the CO group is redistributed amongst the π^* antibonding orbitals of the carbonyl group, then the M-C and C-O bond character are principally determined by the extent of this π bonding. If there is no formal change in the oxidation state of the metal, then the nature of the metal ligand bond is assumed to be controlled by the same mechanism that determines the nature of the metal-carbonyl bond. Metal to metal σ bonding will increase the charge on the transition metal, increase the population of the antibonding π^* orbitals, and decrease the carbonyl stretching frequency. At the same time, any metal to ligand π bonding will remove charge from the metal and increase the carbonyl stretching frequency. Thus the variation in the carbonyl stretching frequencies for a series of compounds will reflect the (σ-π) bonding properties of the ligand.

Various workers have tried to correlate certain physical properties of the ligands with various trends in the carbonyl stretching frequency. Thus it was found that there is a linear, or near linear

correlation between the C.K. force constants and the σ^* Taft polarity constant of the R group is $R_3SnMn(CO)_5$ (220) and $R_3MCo(CO)_4$ (220, 221) (M = Si, Ge, Sn or Pb; R = Me, Et, Ph etc.). A similar linear correlation is found when the Taft σ^* polarity constant is plotted against the carbonyl stretching frequency of a particular mode for the compounds $R_3SnMn(CO)_5$ (R = Me, Et, Ph, or halide), $R_3SiCo(CO)_4$ (R = Et, Ph, Cl, or OMe) $R_3SnRe(CO)_5$ (R = Me, Ph, Cl, or Br) $R_3SnFe(CO)_2cp$ (R = Et, Ph, or halide) and $R_3SnMo(CO)_3cp$ (R = Me, Ph or Cl) (257). In the compounds $Ph_{3-n}Cl_nSnMn(CO)_5$ (52), and $R_{3-n}X_nMCo(CO)_4$ (46) (n = 0 to 3; M = Ge or Sn; X = Cl, Br, or I; and R = Me or Ph), there is a linear correlation between the average CO stretching frequency and the sum of the electronegativities of the group bonding to tin or germanium. For the compounds $Ph_{3-n}X_nSnMn(CO)_5$ (n = 0 to 3; X = Cl, or C_6F_5) it was shown that there is also a linear correlation between the high frequency a_1 mode and the relative sum of the electronegativities of the ligands bonding to tin, from which an estimate of the electronegativity of C_6F_5 was made (52). Similarly, a plot of the dipole moment of the $MCo(CO)_4$ group against the average CO stretching frequency in the compounds $X_3M'Co(CO)_4$ (X = Cl, OMe, or Et; M = Si, Ge or Sn) was also linear (222). Such trends have been explained by assuming that the changes in the carbonyl stretching frequency are due to changes in the σ donor properties of the ligands, the π contribution remaining constant (220). However, although a straight line correlation of some physical parameter with the CO stretching frequency, or better still the force constants, may show that the anharmonicity of the CO vibration, and its coupling to other

vibrations is constant throughout the series, it does not necessarily give an accurate picture of the genuine electron distribution, since any change in frequency of the CO stretching vibration could also arise from slight changes in stereochemistry or metal-ligand σ bond anisotropy.

Of more importance however, is the fact that the changes in the CO stretching frequency are dependent upon the (π-σ) bonding properties of the ligand, which cannot be separated into either σ or π effects. Attempts to relate the force constants k_1 and k_2 to changes in σ or π metal-ligand bonding have in general been unsuccessful since the effect of dπ - pπ, dπ - dπ bonding, or bond anisotropy are difficult to estimate, and the errors in k were too large to rationalise the observed trends. The values of k_1 and k_i have been taken as a direct measure of the π acceptance of a ligand on the express assumption that the σ donor property remains constant (48). However k_1 (and presumably k_i) are proportional to both the σ and π capacities of the ligand and so cannot be used as a probe of one or the other effect. Indeed it is worth noting that there is no dependance of k_i on k_1, and that the value of k_i is remarkably constant over a large range of ligands (48, 52). Graham used the relationship $\Delta k_1 = \Delta\sigma + 2\Delta\pi$, and $\Delta k_2 = \Delta\sigma + \Delta\pi$, where Δk is the change in force constant from the reference compound $MeMn(CO)_5$, and Δσ and Δπ are the change in the σ and π bonding parameters in an attempt to correlate the σ and π characteristics of a variety of ligands L for compounds of the type $LMn(CO)_5$ (223). However, although a general trend of decreasing π acceptance with decreasing σ donation was apparent over a large range of ligands, it

was not apparent for ligands of similar character. Furthermore, in view of the gross assumptions made in calculating k, and in relating its value to any direct consequence of σ or π bonding via the CO stretching frequency, the errors in this method are likely to be so large as to completely obscure the real trend, if indeed there is any.

The data shown in Table 5-1 show that, for a given Group IV atom, the frequency of the high frequency a_1 mode increases as phenyl is replaced by the more electron withdrawing Cl or C_6F_5 groups. This removes the charge from the manganese atom thus leaving less charge to be used in π-bonding with the carbonyl group and hence increases the C-O bond order while decreasing the M-C bond order. The order of electronegativity is Cl>C_6F_5>Ph, but the successive replacement of Ph by Cl or C_6F_5 does not show a particularly linear trend for any series, suggesting that the linear correlation of the high frequency mode with electronegativity for the compounds $Ph_{3-n}X_nSnMn(CO)_5$ (n = 0 to 3; X = Cl or C_6F_5) is fortuitous. It is also remarkable that the frequencies for the compounds $Ph_{3-n}Cl_nSnMn(CO)_5$ are the same as those for $Ph_{3-n}Br_nSnMn(CO)_5$, even though bromine is less electron withdrawing than chlorine and consequently should show lower frequencies in the carbonyl stretching region. The near identical value for the carbonyl stretching frequencies in $Me_2XSnMn(CO)_5$ (X = I or Cl) suggest that the lower inductive effect of iodine is offset by its reduced back-donation to to tin, (223) and presumably the same effect is operating here.

The variation of the frequencies with the variation of M within a given set of ligands shows that the frequency of the highest

frequency a_1 mode generally increase in the order Sn<Si<Ge. For the compounds $Ph_3MMn(CO)_5$ the order is Pb<Sn<Ge<Si but for the compounds $Cl_3MMn(CO)_5$ the order is Si<Sn<Ge. This latter order has also been observed in $Cl_3MCo(CO)_4$ (220) and $Cl_3MFe(CO)_2cp$ (224), and has been attributed to the fact that Ge or Sn are better π acceptors than Si, and that π bonding in the metal-metal bond becomes more important as the Group IV-ligand bonds become more electron withdrawing. However, this could also be due in part to a simple electronegativity effect due to the Group IV atom itself since it is known that depending upon it environment, germanium can be more electronegative than silicon.

However, the presence of π bonding in metal-metal bonds of this type is by no means proven, and these small variations in the carbonyl stretching frequency may not be related to changes in the electronic environment of the metal-metal bond at all, but could be more dependant upon the anharmonicity or state perturbations to which the carbonyl vibrations are subjected. Even considering that the small changes in the carbonyl stretching frequencies or force constants to be related to a composite (σ-π) effect is not very realistic, since the force constants for the series $Cl_3MMn(CO)_5$ (M = Si, Ge or Sn) are all very similar, thus suggesting that these ligands have similar (σ-π) bonding abilities (223). However this similarity is not shown by the Mossbauer studies on some trichloro Group IV metal-ion systems which show that these ligands have very different properties when bonded to iron (157).

Similar trends in the carbonyl stretching frequency are noted for the compounds given in Table 5-2. Once again for a given metal, the frequency increases as the ligands bound to the Group IV atom

become more electron withdrawing in the order Ph<C_6F_5<Br<Cl, while for a given set of ligands around the Group IV atom the frequencies increase in the order Sn<Si<Ge.

For the substituted complexes of the type $Ph_{3-n}Cl_nSnFe(CO)(cp)L$ (L = CO, phosphine or phosphite), the influence of L increases the carbonyl stretching frequency in the order PEt_3<PPh_3<$P(OPh)_3$<CO, and is a measure of the poorer π acceptor properties of these ligands relative to CO.

The better π acceptors tend to leave less charge on the iron atom for π bonding with the carbonyl π^* antibonding orbitals such that population of these orbitals is decreased, but increases the CO bond order and hence the carbonyl frequency. The tendency to remove charge from the iron atom increases in the order PEt_3<PPh_3<$P(OPh)_3$<CO, but is of course a function of both the σ and π properties of the ligands. This order is the same as that deduced from the iron Mossbauer results [Chapter 3 (8)], which indicates that the removal of charge from the iron atom causes an increase in the dishielding of s electrons at the iron nucleus, thus increasing the s density at the nucleus but decreasing the centre shift.

2) Raman Spectra in the Metal-Metal Stretching Region

Whilst infrared spectra have been used extensively to correlate carbonyl stretching modes, they have not been widely used to investigate the region below 200 cm^{-1} where the metal-metal stretching vibrations are expected to occur. This is due mainly to the difficulties of obtaining good routine spectra and, because of the small change in dipole moment resulting from a metal-metal stretching mode, the bands

Table 5-1

Infrared Carbonyl Stretching Frequencies (in cm^{-1}) for the Compounds $Ph_{3-n}X_nMMn(CO)_5$ (n = 0 to 3; X = Cl or C_6F_5; and M = Si, Ge, Sn or Pb) $Ph_{3-n}Br_nSnMn(CO)_5$ and $Cl_n(C_6F_5)_{3-n}SnMn(CO)_5$ (n = 1 or 2)

Compound	a_1'	e	b_1	a_1''[a]	Reference
$Ph_3SiMn(CO)_5$	2002	2002	2029	2097	48
	2003	2003	2030	2098	this work
$Ph_2ClSiMn(CO)_5$	2016	2016	2043	2108	this work
$PhCl_2SiMn(CO)_5$	2024	2022	2055	2116	this work
$Cl_3SiMn(CO)_5$	2035	2035	b	2123	69
$Ph_2(C_6F_5)SiMn(CO)_5$	2014	2009	2041	2107	this work
$Ph(C_6F_5)_2SiMn(CO)_5$	2022	2018	2048	2113	this work
$(C_6F_5)_3SiMn(CO)_5$	2028	2023	2057	2118	this work
	2030	2024	2059	2118	71
$Ph_3GeMn(CO)_5$	2003	2003	2032	2097	48
	2003	2003	2032	2098	this work
$Ph_2ClGeMn(CO)_5$	2010	2020	2048	2109	this work
$PhCl_2GeMn(CO)_5$	2023	2033	2063	2123	this work
$Cl_3GeMn(CO)_5$	2037	2047	d	2130	this work
	2038	2048	b	2130	69
$Ph_2(C_6F_5)GeMn(CO)_5$	2008	2019	2043	2107	this work
$Ph(C_6F_5)_2GeMn(CO)_5$	2020	2026	2050	2115	this work

a) in cyclohexane solution
b) not reported
d) not observed

Table 5-1 cont'd.

Compound	a_1'	e	b_1	a_1''[a]	Reference
$(C_6F_5)_3GeMn(CO)_5$	2023	2028, 2032	2060	2120	this work
$Ph_3SnMn(CO)_5$	2002	2002	2027	2093	48
	2003	2003	2029	2093	this work
$Ph_2ClSnMn(CO)_5$	2018	2018	2044	2103	52
$PhCl_2SnMn(CO)_5$	2031	2023	2058	2113	52
$Cl_3SnMn(CO)_5$	2039	2046	2070[c]	2126	48
$Ph_2BrSnMn(CO)_5$	2018	2018	2053	2105	this work
	2010	2019	b	2106	225
$PhBr_2SnMn(CO)_5$	2025	2032	2043	2115	this work
	2026	2034	b	2116	225
$Br_3SnMn(CO)_5$	2038	2044	d	2125	this work
	2038	2045	2060[c]	2124	48
$Ph_2(C_6F_5)SnMn(CO)_5$	2015	2012	2038	2101	52
	2015	2010	2038	2100	this work
$Ph(C_6F_5)_2SnMn(CO)_5$	2020	2020	2045	2107	52
	2020	2020	2047	2108	this work
$(C_6F_5)_3SnMn(CO)_5$	2029	2025	2059	2116	52
	2034	2029	2059	2116	this work
$Cl_2(C_6F_5)SnMn(CO)_5$	2035	2045	2067	2124	this work
$Cl(C_6F_5)_2SnMn(CO)_5$	2038	2038	2062	2119	this work

c) band not observed; position calculated

Table 5-1 cont'd

Compound	a_1'	e	b_1	a_1''	Reference
$Ph_3PbMn(CO)_5$	2003	2003	2027	2091	48
	2003	2003	2029	2091	this work

Table 5-2

Infrared Carbonyl Stretching Frequencies (in cm^{-1}) and the Chemical Shift of the Cyclopentadienyl Group (in tau values) for the Compounds $Ph_{3-n}X_nMFe(CO)_2cp$ (n = 0 to 3; X = Cl or C_6F_5; M = Si, Ge, Sn or Pb) and $Ph_{3-n}Br_nSnFe(CO)_2cp$

Compound	a'	a"[a]	τ_{cp}[c]	Reference
$Ph_3SiFe(CO)_2cp$	2004	1954	5.13	this work
$Ph_2ClSiFe(CO)_2cp$	2014	1964, 1972 sh	5.04	"
$PhCl_2SiFe(CO)_2cp$	2027, 2023 sh	1980, 1976 sh	4.90	"
$Cl_3SiFe(CO)_2cp$	2039	1995	4.73	"
	2039	1995		224
$Ph_2(C_6F_5)SiFe(CO)_2cp$	2015	1967	5.00	this work
$Ph(C_6F_5)_2SiFe(CO)_2cp$	2026	1977, 1980 sh	4.94	"
$(C_6F_5)_3SiFe(CO)_2cp$	2034	1987	4.94	"
	2029	1982		71
$Ph_3GeFe(CO)_2cp$	2003	1955	5.08	this work
$Ph_2ClGeFe(CO)_2cp$	2016, 2020 sh	1970, 1980 sh	4.97	"
$PhCl_2GeFe(CO)_2cp$	2032, 2027 sh	1992, 1986 sh	4.70	"
$Cl_3GeFe(CO)_2cp$	2049	2005	4.53	"
$(C_6F_5)_3GeFe(CO)_2cp$	2038	1995	4.85	this work
$Ph_3SnFe(CO)_2cp$[b]	1997	1950	4.97	this work
	1995	1944		224
$Ph_2Cl\ SnFe(CO)_2cp$[b]	2014	1966	4.77	this work

a) in cyclohexane solution
b) in $CHCl_3$ solution
c) in $(CD_3)_2CO$ solution

Table 5-2 cont'd

Compound	a'	a''[a]	ν_{cp}[c]	Reference
$PhCl_2SnFe(CO)_2cp$[b]	2030	1986	4.57	this work
$Cl_3SnFe(CO)_2cp$[b]	2050	2010	4.45	"
	2048	2008		224
$Ph_2BrSnFe(CO)_2cp$[b]	2010	1963	4.77	this work
$PhBr_2SnFe(CO)_2cp$[b]	2028	1983	4.60	"
$Br_3SnFe(CO)_2cp$[b]	2047	2005	4.47	"
$Ph_3SnFe(CO)_2cp$	1999	1951	4.97	this work
$Ph_2(C_6F_5)SnFe(CO)_2cp$	2011, 2000 sh	1965, 1953 sh	4.92	"
$Ph(C_6F_5)_2SnFe(CO)_2cp$	2023	1982	4.82	"
$(C_6F_5)_3SnFe(CO)_2cp$	2029	1988	4.77	"
$Ph_3PbFe(CO)_2cp$	1976	1955	4.90	this work

Table 5-3

Infrared Carbonyl Stretching Frequencies (in cm^{-1}) and the Chemical Shift of the Cyclopentadienyl Group (in tau values) for the Compounds $Ph_{3-n}Cl_nSnFe(CO)_{2-x}(cp)L_x$ [n = 0 to 3 for x = 0; x = 1 and L = PPh_3, PEt_3 and $P(OPh)_3$; x = 2 and L = $P(OPh)_3$ and n = 3 for x = 1 L = $P(OEt)_3$]

Compound	νCO[a]	τ_{cp}[b]	Multiplicity
$Ph_3SnFe(CO)_2cp$	1997, 1950	5.29	singlet
$Ph_3SnFe(CO)(cp)PPh_3$	1913, 1924 sh	5.67	doublet
	1911, 1923 sh[c]		
$Ph_3SnFe(CO)(cp)PEt_3$	1905	5.52	doublet
$Ph_3SnFe(CO)(cp)P(OPh)_3$	1940	5.74	doublet
$Ph_3SnFe(cp)[P(OPh)_3]_2$	---	5.69	triplet
$Ph_2ClSnFe(CO)_2cp$	2014, 1966	5.12	singlet
$Ph_2ClSnFe(CO)(cp)PPh_3$	1932	5.48	doublet
$Ph_2ClSnFe(CO)(cp)PEt_3$	1924	5.36	doublet
$Ph_2ClSnFe(CO)(cp)P(OPh)_3$	1957	5.62	doublet
$Ph_2ClSnFe(cp)[P(OPh)_3]_2$	---	5.66	triplet
$PhCl_2SnFe(CO)_2cp$	2030, 1986	4.96	singlet
$PhCl_2SnFe(CO)(cp)PPh_3$	1949	5.32	doublet
$PhCl_2SnFe(CO)(cp)PEt_3$	1945	5.30	doublet
$PhCl_2SnFe(CO)(cp)P(OPh)_3$	1972	5.59	doublet
$PhCl_2SnFe(cp)[P(OPh)_3]_2$	---	5.61	triplet

a) in $CHCl_3$ solution
b) All J_{P-H} 1.5 c/s
c) in cyclohexane solution, reference 114

Table 5-3 cont'd

Compound	ν_{CO}[a]	τ_{cp}[b]	Multiplicity
$Cl_3SnFe(CO)_2cp$	2050, 2010	4.94	singlet
$Cl_3SnFe(CO)(cp)PPh_3$	1973	5.28	doublet
	1969[b]		
$Cl_3SnFe(CO)(cp)PEt_3$	1968	5.22	doublet
$Cl_3SnFe(CO)(cp)(POPh)_3$	1996	5.54	doublet
$Cl_3SnFe(cp)[P(OPh)_3]_2$	---	5.61	triplet
$Cl_3SnFe(CO)(cp)P(OEt)_3$	1985	5.55	doublet

may be unexpectedly weak. With the availability of laser Raman spectrometers, low frequency vibrational spectra are easy to obtain both for solid and solutions and give strong bands that can be directly assigned to metal-metal stretching vibrations. Furthermore, since all these vibrations contain at least one mode of A_1 symmetry, these modes can be unambiguously assigned on the basis of polarisation data. Certain metal cluster compounds give a band pattern in the metal-metal region that can be used as a diagnostic tool in elucidating the structure of compounds of this type (7), although close agreement of the observed spectra with the one predicted on the basis of symmetry cannot be taken as conclusive proof of their structure.

Values for the metal-metal stretching force constant k_{MM} can only be satisfactorily obtained by a total force field analysis of all the fundamental modes of a compound of known structure (7). Where the structure is not known it can sometimes be assumed to be analogous to compounds of known structure, or deduced from the analysis of the carbonyl stretching frequencies. However, there are relatively few compounds that exhibit more than the minimum number of fundamental modes, or have a small enough force field for accurate vibrational analysis. Therefore some estimates of k_{MM} have been made by considering the metal-metal stretch as a localised mode and free of any appreciable mixing with other modes. Although this method may be used to give an indication of the value of k_{MM} for systems of widely differing bond strengths, it is obvious that for systems that are closely related this method, more often than not, gives misleading values for k_{MM} and cannot be used to interpret small differences

in bond strength (7).

Full vibrational analysis studies have been carried out on the systems $Cl_3MCo(CO)_4$ (M = Si, Ge,or Sn) (206), $X_3MCo(CO)_4$ (X = Br or I; M = Ge or Sn) (226) and $M[Co(CO)_4]_2$ (M = Zn, Cd,or Hg) (227), while the system $X_3SnMn(CO)_5$ (X = Cl, Br,or Me) (228) was analysed on the basis of infrared spectra alone.

The analysis of the system $Cl_3MCo(CO)_4$ (206) shows that consideration of the metal-metal stretching frequency to be soley due to the masses of M and Co gives k_{MM} values of the right magnitude but in the wrong order. On the other hand, consideration of the whole molecule as a simple diatomic oscillator consisting of Cl_3M and $Co(CO)_4$ gives k_{MM} values of both the wrong order and magnitude. Analysis of the corresponding bromo and iodo species (226) shows that the metal-metal force constant for the chloro derivative is twice that of the iodo derivative,and for a given substituent on M the force constants increase in the order Sn>Ge. Thus, although the mass of X and M can affect the value of k_{MM}, other factors such as the better π acceptor ability of Cl_3Sn relative to Cl_3Ge and the effect of any M-X π characture must also be taken into account. Furthermore the analysis of the compounds $M[Co(CO)_4]_2$ (227) show that while differences in the M-Co force constant would be expected on the basis of electronic or simple molecular orbital treatments, the force constants are nearly identical for these compounds and do not show the trend that was deduced from examination of the mass spectral fragmentation patterns (229).

It is clear that in all the above compounds and in $X_3SnMn(CO)_5$

(228) the mixing of the metal-metal stretching mode with other modes is proportional to both the masses of X and M. The amount of mixing decreases as the mass of M increases, and increases as X increases. However, when X is lighter than chlorine, and M is about the same mass as tin, the value of k_{MM} can be fairly accurately predicted using only the masses of the metal atoms (206). A further refinement (16) is to take into consideration all the groups lying along the direction of the metal-metal bond such that for $Mn(CO)_5$ and $Co(CO)_4$ derivatives, the mass of the axial carbonyl group is added to the mass of Mn or Co which is then treated as a single atom. This method predicts the force constant of $Cl_3SnCo(CO)_4$ to be 1.22 mdynes/Å which is very close to the value of 1.23 mdynes/Å found by normal coordinate analysis, but the agreement for compounds of the type $M_2(CO)_{10}$ (M = Mn, Re and Tc) (230, 231) in Table 5-4 is not as good, although this method predicts both the magnitude and relative order of the metal-metal stretching force constants. However, for the compounds $X_3SnMn(CO)_5$, better agreement between the values calculated on the above basis and those obtained from normal coordinate analysis are obtained if the effect of the axial carbonyl is ignored and the Sn-Mn stretching mode is treated as a simple diatomic involving just the masses of the two atoms forming the metal-metal bond.

It is worth noting that the value of k_{MM} for $Cl_3SnCo(CO)_4$ is higher than that for $Cl_3SnMn(CO)_5$, and this is the reverse of what would be expected on the basis of chemical evidence and from the Mossbauer spectra. A comparison of the chemical reactivities of the tin-manganese and tin-cobalt bonds, shows that the latter is by far

Table 5-4

Comparison of the Metal-Metal Stretching Force Constants (k_{MM}) for the Compounds $M_2(CO)_{10}$, $X_3SnMn(CO)_5$ and $Cl_3SnCo(CO)_4$

Compound	ν(M-M) cm^{-1}	Force Constant k_{mm} (mdynes/Å) Axial CO Included	Axial CO Ignored	Normal Coordinate Analysis	Reference
$Cl_3SnCo(CO)_4$	204	1.22	0.97	1.23	206
$Cl_3SnMn(CO)_5$	197	1.11	0.86	1.00	228
$Me_3SnMn(CO)_5$	179	0.92	0.71	0.70	228
$Mn_2(CO)_{10}$	160	0.62	0.41	0.59	230
$Tc_2(CO)_{10}$	148	0.81	0.63	0.72	230
$Re_2(CO)_{10}$	122	0.93	0.90	0.82	230
$MnRe(CO)_{10}$	157	0.87	0.82	0.81	230

the weaker, and susceptible to cleavage even by the most mild reagents (30). The Mossbauer data (141) shows that $Mn(CO)_5$ is a better σ donor than $Co(CO)_4$ and hence should form a stronger bond to tin. The reason as to why this is not reflected in the value of k_{MM} is not clear, but as has been pointed out (245, 258), force constants in general need not have any particular physical significance, even when calculated by the most rigourous methods available.

In compounds containing one metal-metal bond the metal-metal stretching frequency will be totally symmetric and will hence be strongly polarised. In addition, the very polarisable metal-metal bond will give rise to a large change in polarisation during its vibration and will be expected to give a medium to strong band in the Raman spectra. The metal-metal stretching frequencies for some of the tin-transition metal species, presented in Table 5-5, were assigned on their intensity, their expected position from other work, and for $Ph_3SnMn(CO)_5$ and $Ph_3SnFe(CO)_2cp$ on the basis of polarisation measurements. For some of the coloured compounds extensive decomposition took place and only a very weak peak at about 200 cm^{-1} was observed, which was nevertheless assigned to the metal-metal stretching vibration.

In addition to the metal-metal stretching frequency, the compounds containing the $Mn(CO)_5$ moiety also exhibited bonds in the range 110 to 122 cm^{-1} and between 70 and 85 cm^{-1} which were assigned to the C-Mn-C and SnX deformation respectively. The tin-halogen stretching vibrations for $Cl_3SnMn(CO)_5$ and $Br_3SnMn(CO)_5$ could be unambiguously assigned at 349 cm^{-1} and 249 cm^{-1} respectively, and are in agreement with the

infrared spectra (228). For the other phenylhalotin compounds, the the assignment of these vibrations is not as clear due to their reduced intensity, and for the phenylbromotin compounds in particular, could be confused with various tin-phenyl deformations which also appear in the region 200 to 250 cm^{-1} (231). The strong bands that were always present at 640 to 660 cm^{-1} were assigned to the Mn-CO deformations, while those around 400 cm^{-1} were assigned to the Mn-C stretching vibrations. For compounds containing the phenyl group, there was in addition to the weak b nds between 200 and 250 cm^{-1} a very strong band at 1000 cm^{-1} which was assigned to the ring breathing mode. By contrast $(C_6F_5)_3SnMn(CO)_5$ did not exhibit a band of similar intensity although there were a number of bands in the region 300 to 600 cm^{-1} that could be presumably assigned to various ring stretching and bonding modes, characteristic of the C_6F_5 group. The assignment of the metal-metal stretching frequency for these derivatives was also complicated by its close proximity to other strong bonds below 200 cm^{-1}. $Ph_2(C_6F_5)SnMn(CO)_5$ still exhibited a very strong bond at 183 cm^{-1}, but for $Ph(C_6F_5)_2SnMn(CO)_5$ and $(C_6F_5)_3SnMn(CO)_5$ there was no strong bond that could be unambiguously assigned to the metal-metal stretching frequency. Since some of the bonds in this region e.g. the CO-M-CO deformation mode are also polarised, the assignment of the metal-metal stretching frequency could not be made on the basis of polarisation measurements, and hence was made from their expected position. They thus could be in error, and in any event are more extensively coupled to other vibrations than those for the other derivatives.

From the data in Table 5-5, the replacement of phenyl by chlorine

increases the metal-metal frequency, but the replacement of phenyl by bromine reduces this increase, such that for $PhBr_2SnFe(CO)_2cp$ and $Br_3SnFe(CO)_2cp$, the frequency is actually less than for $Ph_3SnFe(CO)_2cp$. The replacement of phenyl by pentafluorophenyl, or the replacement of tin by lead, reduces the frequency and could very well be a manifestation of the increase in mass of these groups. It is also worth noting that an increase in the metal-metal stretching frequency is accompanied by an increase in the halogen tin stretching frequency, and that for the same type of compound, the stretching frequency of the tin-iron bond is greater than that of the tin-manganese bond. This could be partly due to the decrease in the mass of the $Fe(CO)_2cp$ group over that for $Mn(CO)_5$, but as this difference is not very great, it is more probably due to an increase in the mixing in of other modes such as the cyclopentadienyl bending modes into the metal-metal stretching mode.

The substitution of a carbonyl group in $Ph_3SnFe(CO)_2cp$ by triphenylphosphite increases the frequency, in accordance with the increase observed in the system $Me_3SnMn(CO)_4L$ over that for $Me_3SnMn(CO)_5$, (16) but the disubstituted complex $Ph_3SnFe(cp)[P(OPh)_3]_2$ shows a decrease in the metal-metal stretching frequency. This could be again due to a mass effect, which for the disubstituted complex is great enough to mask any increase in the strength of the metal-metal bond that results from the introduction of two phosphite ligands.

Clark et al (233) have attempted to explain the observed trends in the metal-metal frequencies for a number of methyl tin transition

metal species. However it is not correct to assume that even in these systems the metal-metal stretching frequency is just related to the masses of the metal atoms, since it has been shown that for the system $X_3SnMn(CO)_5$ (X = Cl, Br or Me) (228) the order for the values of the metal-metal force constant k_{MM} increase in the order Me<Br<Cl, although the frequencies themselves increase in the order Me<Br<Cl. This is due to the extensive mixing of the metal-metal with the tin bromine stretching frequency for $Br_3SnMn(CO)_5$ which raises the observed value for the tin manganese stretching vibration. The purity of any given mode can be evaluated from a potential energy distribution table, and for the compounds $X_3SnMn(CO)_5$, the purity of the Sn-Mn stretch is 68% for X = Cl, 64% for X = Me, but only 46% for X = Br. This again emphasises the fact that the purest metal-metal stretching vibrations can only be expected when X is lighter than chlorine, and even in this situation the metal-metal stretching frequency is still appreciably mixed with the C-Mn-C deformation mode.

Another interesting point is that the force field elements for the transition metal species for the compounds $X_3MCo(CO)_4$ (X = Cl, Br or I; M = Si, Ge or Sn) (206, 226) are identical,and only the elements that relate to the metal-metal or metal halogen vibrations change at all. In addition,the calculated frequencies for the carbonyl stretching vibrations in $Cl_3MCo(CO)_4$ (206) and $X_3SnCo(CO)_4$ (X = Br or I) (226) are the same even though there are differences in the observed spectra. For the compounds $X_3SnMn(CO)_5$ only the elements for the X-Sn and Sn-Mn vibrations changed significantly (228), although in this study the value of the carbonyl stretching force constants for X = Me

were substantially lower than those for X = Cl or Br.

According to Risen et al (227), differences in the carbonyl stretching frequencies of less than 10 cm^{-1} are insufficient criteria for assessing the nature of the metal-metal bond. Changes in the CO force constant from compound to compound based upon a change in the CO stretching frequency of 10 cm^{-1} will change the calculated frequencies such that an exact fit between the observed and calculated frequencies can be obtained, but the vibrations then become less harmonic. This however, has little effect upon k_{MM} and a shift of 10 cm^{-1} is what would be expected on going from the solution to the vapour state where the oscillations are more harmonic, and presumably a better indication of changes in the metal-CO and metal-metal bond.

3) Proton Nuclear Magnetic Resonance Studies

A characteristic feature of the $Fe(CO)_2cp$ group is the single sharp resonance of the π-C_5H_5 ring in which all the protons are equivalent. For compounds containing a metal-metal bond the position or chemical shift of this resonance is dependent on a) the Group IV atom bonding to iron, b) the ligands bonding to this atom, and c) on the nature of the other ligands bonding to iron. The position of the cyclopentadienyl resonance is also very dependent upon the solvent which, as for carbonyl infrared spectra, must be kept constant if valid comparisons are to be made. The chemical shift of the cyclopentadienyl group is dependent upon the degree of shielding of the protons in the ring. More negative charge on the iron atom will cause an increase in both the electron population of the Group IV-iron bond and in the population of the cyclopentadienyl ring antibonding

Table 5-5

The Metal-Metal Stretching Frequencies (in cm^{-1}) for some Tin-iron and Tin-manganese compounds in the Solid State

Compound	ν(M-Fe)	Compound	ν(M-Mn)	ν(M-X)
$Ph_3SnFe(CO)_2cp$	205	$Ph_3SnMn(CO)_5$	172	
	201 sol. polarised		170 soln. polarised	
	174 I.R. Nujol mull[a]		175 I.R. mull[a]	
			170 I.R. soln.[b]	
$Ph_2ClSnFe(CO)_2cp$	209			
$PhCl_2SnFe(CO)_2cp$	221	$Ph_2ClSnMn(CO)_5$	181	315
$Cl_3SnFe(CO)_2cp$	224	$PhCl_2SnMn(CO)_5$	197	328
$Ph_2BrSnFe(CO)_2cp$	208	$Cl_3SnMn(CO)_5$	200	349
$PhBr_2SnFe(CO)_2cp$	204		201 I.R. mull[a]	
$Br_3SnFe(CO)_2cp$	201			
$Ph_2(C_6F_5)SnFe(CO)_2cp$	204		197 I.R. soln.[b]	345
$Ph(C_6F_5)_2SnFe(CO)_2cp$	198	$Ph_2BrSnMn(CO)_5$	177	230
$Ph_3PbFe(CO)_2cp$	199	$PhBr_2SnMn(CO)_5$	179	238
$Ph_3SnFe(CO)(cp)\ P(OPh)_3$	214	$Br_3SnMn(CO)_5$	185	249
$Ph_3SnFe(cp)[P(OPh)_3]_2$	202		178 I.R. soln.[b]	240
		$Ph_2(C_6F_5)SnMn(CO)_5$	183	
		$Ph(C_6F_5)_2SnMn(CO)_5$	157?	
		$(C_6F_5)_2SnMn(CO)_5$	121?	
		$Ph_3PbMn(CO)_5$	163	

a) Reference 233
b) Reference 228

orbitals. This latter effect will result in an increase in the shielding of the ring protons and will be reflected by an increase in their chemical shift.

For a given set of ligands around the Group IV atom, electron donation to the iron atom decreases in the order Si>Ge>Sn>Pb, such that silicon compounds would be expected to have the highest chemical shift, as is observed. However this effect is decreased by the introduction of more electronegative groups, such that for a given metal the decrease in chemical shift for a given ligand is in the order $Ph>C_6F_5>Br>Cl$. Thus the chemical shift of the cyclopentadienyl group is dependent upon the (σ-π) properties of the organo Group IV species. Groups such as Ph_3Si which have little π acceptance properties, can be considered as σ donors and will have the highest shift, while groups such as Cl_3Sn act as σ donors and π acceptors and will have the lowest shift. It is worth noting that while the bonding abilities of the carbonyl and cyclopentadienyl groups are explained in terms of their (σ-π) contributions, the iron Mossbauer centre shifts in Table 3-5 are related to the (σ+π) bonding abilities, and thus should show a decrease in centre shift with the more electron donating ligands. This is in fact what is observed; the centre shift for $Ph_3SiFe(CO)_2cp$ being the lowest while that for $Cl_3SnFe(CO)_2cp$ is the highest. [Chapter 3 (8)].

The similarity of the bonding properties of the carbonyl and cyclopentadienyl groups have been presented in graphical form by King (234). The more electron donating ligands will cause an upfield shift of the cyclopentadienyl ring resonance but at the same time, some

of the charge on the iron atom will be delocalised into the π antibonding arbitals of the CO group and will decrease the CO bond order, and hence its stretching frequency. For a very wide range of ligands there is an approximately linear relationship between the chemical shift of the cyclopentadienyl ring and the carbonyl force constants. There is however, quite a wide variation of points about the best straight line and this could be in part due to a variation of the solvents used. The range of these variables encountered for metal-metal bonded derivatives is quite small, and from this work a plot of the chemical shift of the cyclopentadienyl ring against the carbonyl stretching force constant gives, in most cases, a shallow curve thus suggesting no real correlation between the two quantities.

Newlands et al (51) have shown that for $Ph_{3-n}Cl_nSnFe(CO)_2cp$ (n = 0 to 3), there is a linear correlation between the chemical shift of the cyclopentadienyl ring and the infrared C-H bonding mode. Although there may be some correlation between the two properties, it is difficult to see why this should be linear and this observation is probably entirely fortuitous. In addition, the C-H bonding mode at about 850 cm^{-1} is extremely weak in both the Raman and infrared spectra and is only easily observed in the solid state. It is thus susceptible to solid state effects, which need not have any direct bearing on the electronic properties of the cyclopentadienyl or carbonyl groups themselves. Attempts have also been made to correlate the chemical shift of the cyclopentadienyl ring with the Taft σ^* polarity constant, but while a reasonable correlation between these two parameters was found for the compounds of the type $RFe(CO)_2cp$

($R = Cl, CF_3, CH_3CO_2, Et, C_3H_7$), it was not very satisfactory for compounds containing a tin-iron bond. An even poorer correlation was found for the compounds $R_3SnMo(CO)_3cp$ (257).

Although good correlations are found between the carbonyl stretching frequency and the Taft σ polarity constant (257), the rather unsatisfactory relationship between the latter and the chemical shift of the cyclopentadienyl ring suggests that there are other factors that control these shifts, and are not necessarily dependent upon the σ or π properties of the organometal group itself.

The very small increase in the chemical shift of the cyclopentadienyl ring upon the introduction of a second phosphine or phosphite group has been explained by assuming that the population of the antibonding orbitals of the cyclopentadienyl ring are almost completely saturated with the introduction of one phosphine or phosphite ligand, such that the introduction of a second molecule has little effect upon the chemical shift of the cyclopentadienyl ring (115). The excess charge left on the iron atom is then presumably removed by increasing the electron density of the metal-metal bond and thus increasing the metal-metal stretching frequency more markedly than the introduction of only one phosphine or phosphite ligand.

Although a substantial increase in the Sn-Mn stretching frequency is observed between the compounds $Me_3SnMn(CO)_4L$ and $Me_3SnMn(CO)_3L_2$ (16), a decrease in the Sn-Fe stretching frequency was observed between $Ph_3SnFe(CO)cpP(OPh)_3$ and $Ph_3SnFecp[P(OPh)_3]_2$ [Chapter 5 (2)]. The increase in the metal-metal stretching frequency for the tin manganese compounds could be a result of an increase in coupling of

the Sn-Mn vibration with other modes such that the purity of this mode is less than that for the monosubstituted or unsubstituted compounds. The Mossbauer spectra on the tin-iron compounds indicate that the change in the electronic environment of the Sn-Fe bond is very small, and its magnitude is not consistent with the magnitude inferred from the vibrational spectra.

4) The Manganese Nuclear Magnetic Resonance Spectra of the Compounds $LMn(CO)_5$

The N.M.R. spectra of manganese compounds have received little attention since most of the readily available compounds are either paramagnetic or have such large line widths that the resonance will not be observed. However, all the derivatives of manganese in the form $LMn(CO)_5$ are diamagnetic and show an appreciable range in their chemical shifts (225, 235, 236) from which it should be possible to deduce information about the manganese-ligand bond. These studies are made more attractive by the fact that sharp resonance signals can be expected from a metal atom situated in an octahedral field such that the chemical shift can be obtained to a high degree of accuracy. However, for nuclei whose nuclear spin is greater than or equal to unity, broadening of the resonance is expected due to nuclear quadrupole coupling. Thus for manganese where the nuclear spin is 5/2, the sharp resonance resulting from a nuclear environment about the manganese atom can be considerably broadened by the nuclear quadrupole induced relaxation of the magnetic resonance. There are only three reports of some studies of the manganese N.M.R. in the literature but as will be seen below, meaningful interpretations

about the origin of the chemical shift are very difficult to obtain.

It is generally accepted that the paramagnetic shift term σ_p is the main factor that controls the chemical shift of the transition elements, such that for a t_{2g}^{6} electron system of C_{4v} symmetry this may be approximated by:

$$\sigma_p = -\frac{4\beta^2}{3}\langle r\rangle^{-3}\left[\frac{8}{\Delta E_1}+\frac{4}{\Delta E_3}+\frac{12}{\Delta E_4}\right]$$

where ΔE the excitation energy for each allowed transition, r is the electron nuclear distance taken over the manganese 3d function, and β is the nuclear magneton (235). While the value of r can only be estimated in a very approximate manner, the excitation energy ΔE, can in theory be found from the d-d bonds observed in the U.V. spectra. However, for derivatives of the type $LMn(CO)_5$ these bands are obscured by the very intense charge transfer bands associated with the $Mn(CO)_5$ species, and are consequently not available. It is for this reason that it is not possible to determine whether, and to what extent, the paramagnetic chemical shift term is dependent on ΔE or r, and only a purely qualitative approach can be taken.

In order to determine whether or not the metal-metal bond was dissociating in solution the spectra of $Ph_3SnMn(CO)_5$ was run in various solvents of as widely differing polarity as possible. The consistancy of the single absorption at about 2510 ppm upfield from aqueous $KMnO_4$ showed that no dissociation was occuring and probably does not occur to any great extent in the other derivatives.

Calderazzo *et al* (235) considered that for the halide derivatives of $Mn(CO)_5$, if the metal halogen bond strengths increase in the order

Cl<Br<I and r remains effectively constant, then the energy difference between the manganese orbitals will be represented by an increase in the value of ΔE. Thus the value of the σ_p term will decrease in the order Cl>Br>I, but will give the order of decreasing chemical shift as I>Br>Cl, as observed.

Alternatively, Onaka et al (225) considered that while ΔE or r do affect the chemical shift quite substantially, it is the change in the amount of mixing of the metal d orbitals used in forming a metal-ligand bond that controls the value of the chemical shift in a series of structurally related compounds. Thus the chemical shift can be taken as a reliable measure of the σ polarity of the ligand-manganese bond, and is complementary to the previous ideas of Calderazzo. Thus the manganese-ligand bond is most ionic in $ClMn(CO)_5$, but becomes more covalent in $Me_3SnMn(CO)_5$, and is most covalent in $Mn_2(CO)_{10}$.

If we consider that it is the change in the σ polarity of the metal-ligand bond that is controlling the chemical shift, then the data presented in Table 5-6 show that the Group IV-manganese bond becomes less polar as more electron-withdrawing groups are bonded to the Group IV atom. For a given set of ligands the order of increasing σ polarity (or decreasing σ donor strength) increases in the order Ge<Sn<Si. However, this order is not necessarily an indication of the metal-metal bond strength, since for the derivatives $Ph_3MMn(CO)_5$ the order of the chemical shift would indicate that the metal-metal bond strength is decreasing in the order Sn>Si>Ge>Ph. This is incompatible with the measurement of the metal-metal bond strengths in the series $Me_3MMn(CO)_5$ by mass spectrometry (44) which shows that if

anything, the order of increasing metal-metal bond strength is M = Pb<Sn<Si<Ge. A similar order for the increase in the importance of metal-metal π bonding (and hence presumably metal-metal bond strength) is also inferred from a study of the carbonyl stretching frequencies, such that the amount of metal-metal π bonding increases with the substitution of more electronegative groups around the Group IV atom (220, 224). However, a full force field analysis of the closely comparable system $Cl_3MCo(CO)_4$ (M = Si, Ge or Sn) show that the value of the metal-metal stretching force constant k_{MM} increases in the same order as the manganese chemical shift for the system $Cl_3MMn(CO)_5$ i.e. Ge<Sn<Si, even though the carbonyl stretching frequencies themselves suggest that π bonding is at a maximum for the germanium derivative. If we assume that k_{MM} is a more reliable measure of metal-metal bond strength than are the carbonyl stretching frequencies, then because of the great similarity between the two series of compounds, a similar order is to be expected for the $Mn(CO)_5$ derivatives. This serves to support the evidence that from the chemical shift data the germanium-manganese bond is more ionic, and hence is possibly weaker than the silicon or tin-manganese bonds.

Although the manganese chemical shift may not be attributed solely to the σ polarity of the metal-metal bond, and the model used is probably a gross oversimplification, it does appear that the chemical shift of the manganese atom is dependent upon the $(\sigma+\pi)$ bonding properties of the Group IV ligand but is mainly dominated by the σ effect.

The observed correlation between the carbonyl stretching

frequencies and the manganese chemical shift for the series $R_{3-n}X_nSnMn(CO)_5$ (R = Me or Ph; X = Cl or Br and n = 0 to 3) (225) and for the series $(C_6F_5)_{3-n}Ph_nSnMn(CO)_5$ (n = 0 to 3) in this work appears to be entirely fortuitous since no such linear correlation exists for the series $Ph_3MMn(CO)_5$, $(C_6F_5)_3MMn(CO)_5$, $Cl_3MMn(CO)_5$ (M = a Group IV metal), or $(C_6F_5)_{3-n}Cl_nSnMn(CO)_5$ (n = 0 to 3). However, a very general correlation between the chemical shift of the manganese nucleus and the highest carbonyl stretching frequency is that as the Group IV ligand becomes a better donor, the electron density on the manganese atom becomes greater, and the chemical shift of the manganese atom increases.

Because CO is a better π acceptor than L, the effect of the increased charge on the manganese atom is to lower the carbonyl stretching frequency. Since it is commonly assumed that the carbonyl stretching frequency is determined mainly by π effects (212), or both σ and π effects (237), changes in the Group IV metal could drastically alter either the σ or π bonding characteristics in a rather unpredictable manner, such that not really suprising that there is no general correlation between the carbonyl stretching frequency and the chemical shift. However, there is a remarkably good linear correlation between Grahamb σ parameter (223) and the chemical shift, and this is shown in Figure 5-5. If the σ parameter is a correct indication of the σ bonding properties of a ligand, then this shows that the chemical shift is dominated by σ effects, and not by π effects since in this case, there is no such correlation between Graham's π parameter (223) and the chemical shift. The

A Plot of Graham's σ Parameter versus the ^{55}Mn Chemical Shift in ppm upfield from $KMNO_4$ for the Compounds $LMn(CO)_5$

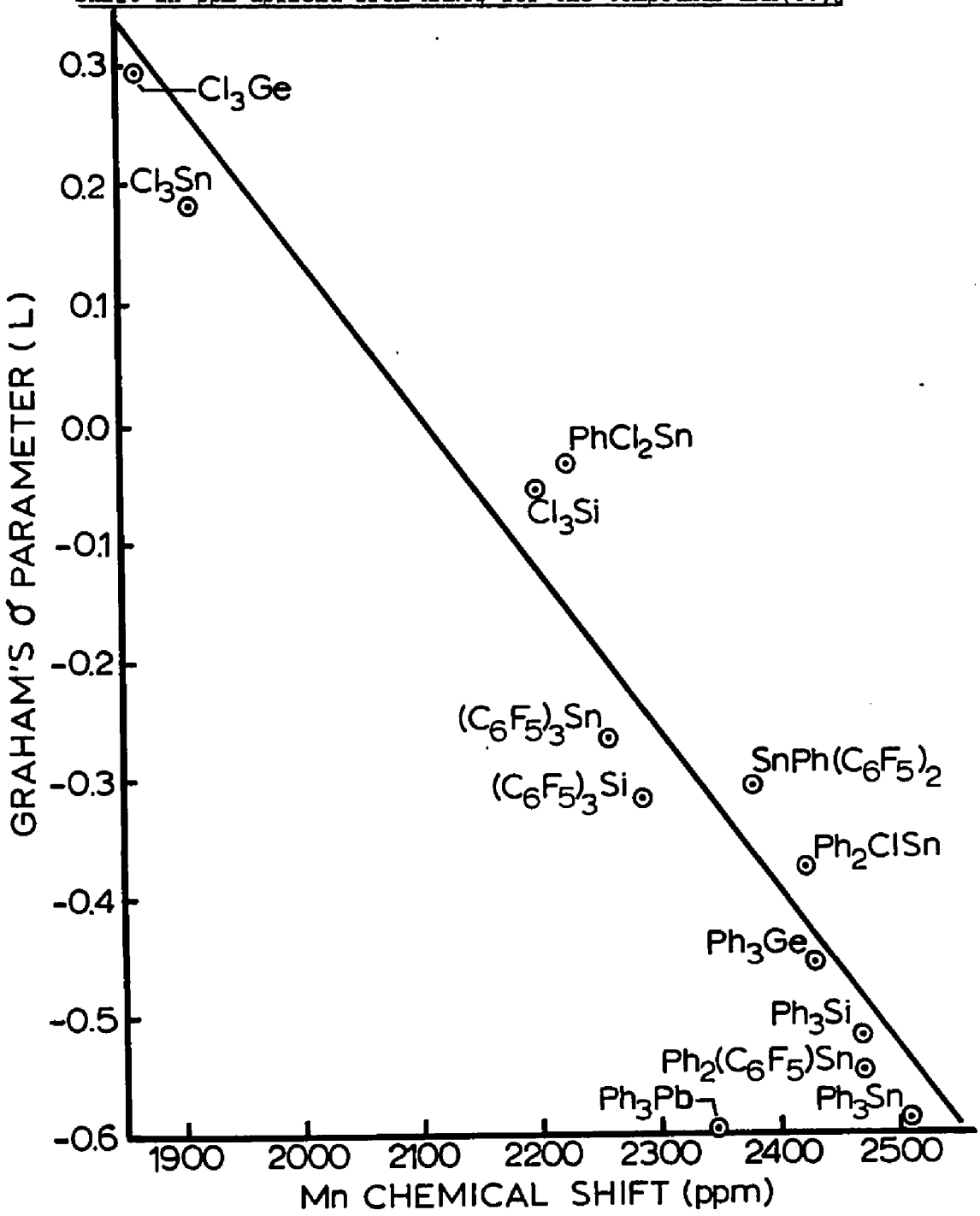


Figure 5-5

exact physical meaning of this result is rather difficult to assess since the σ parameter was determined by an arbitary procedure, and may not be indicative of a pure σ effect at all.

A more interesting feature of these spectra is the variation of the line width with the nature of the Group IV ligand. For the ligands Cl_3M and $(C_6F_5)_3M$, the line widths are very narrow but are considerably broadened for Ph_3M. For the series $Ph_n(C_6F_5)_{3-n}SnMn(CO)_5$ (n = 0 to 3) there is a near linear correlation between the chemical shift and the square root of the line width and as shown in Figure 5-6. A similar variation of the line width with chemical shift has also been observed for some other derivatives of $Mn(CO)_5$ (225, 236), and since exchange phenomena are considered unlikely, these effects have been ascribed to an increase in the nuclear quadrupole coupling of the manganese nucleus. Another factor that could influence the mechanism of quadrupole relaxation, and hence increase the line width, is the rotation of the substituents on the Group IV atom about the metal-carbon or metal halogen axis. For the larger halo or pentafluorophenyl groups, it is possible that these ligands are not free to rotate about their respective bonds to the Group IV metal and hence will give sharper lines. It is not possible to distinguish between the effects of line broadening by nuclear relaxation in the manganese atom, or by steric effects in the ligand, without variable temperature data, but if, as in the case of $XMn(CO)_5$ (X = halide or Me) (235) and $HMn(CO)_{5-x}(PF_3)_x$ (x = 0 to 5) (236), the line widths are controlled mainly by an electronic relaxation mechanism, then some interesting correlations between these line widths and some

A Plot fo the Chemical Shift in ppm upfield from MnO_4 versus the Square Root of the Line Widths for the Series $Ph_{3-n}(C_6F_5)_nSnMn(CO)_5$ (n = 0 to 3)

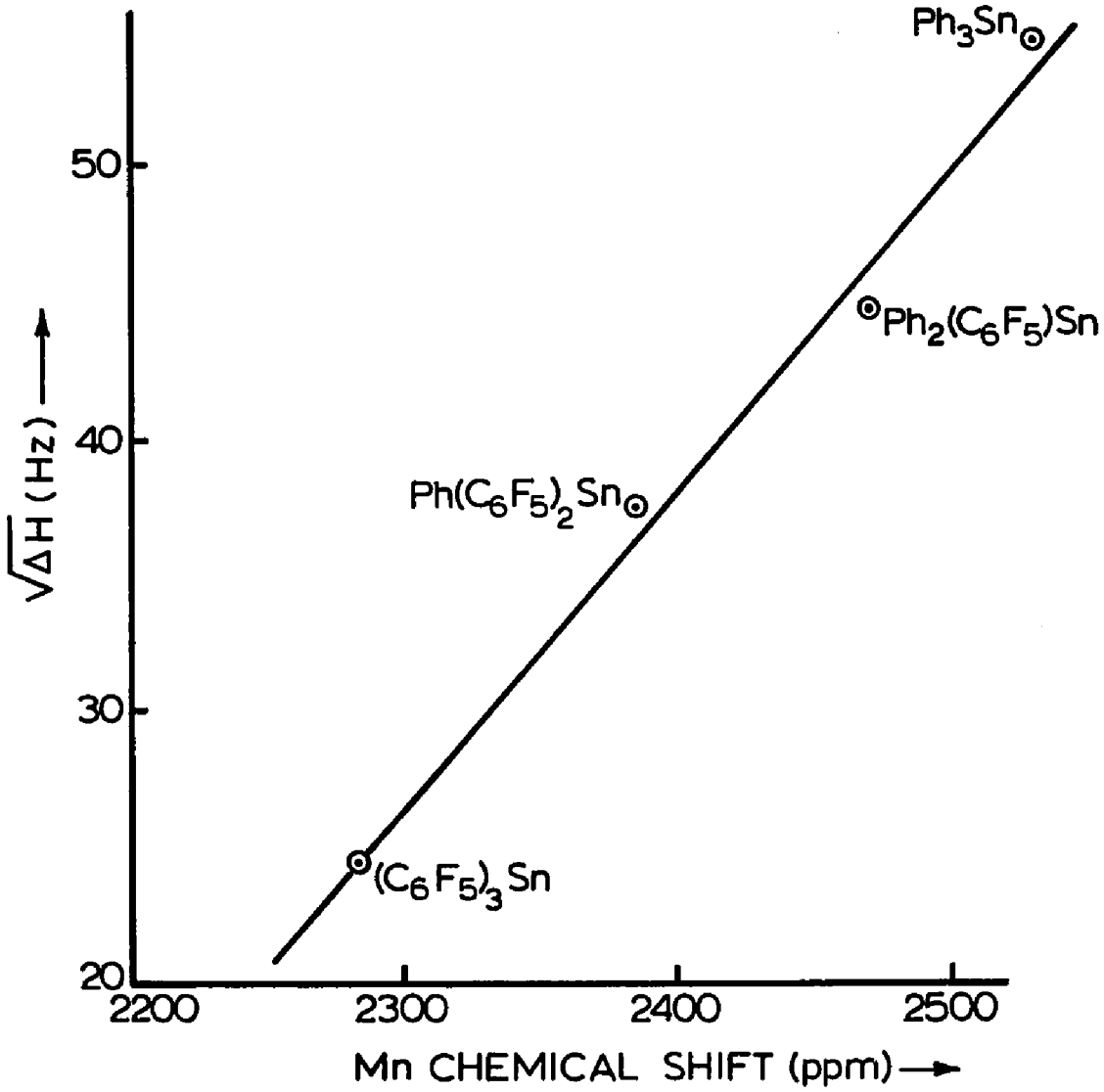


Figure 5-6

Mossbauer data on some other isoelectronic d^6 systems can be made.

The line width ΔH of a nuclear magnetic absorption is determined by the principle field gradient at the magnetic nuclei eq, the correlation time Tc, and the assymmetry parameter η, and is given by the equation:

$$\Delta H = c\left(1 + \frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2 Tc$$

where c is a constant, and eQ the quadrupole moment of the nuclei.

In systems of the type $LMn(CO)_5$ which have nominally C_{4v} symmetry, the assymmetry parameter is zero, and because the molecular size is nearly constant and the measurements were performed in a single solvent at an approximately equal concentration then the correlation time Tc can be considered to be effectively constant. Thus the root of the line width is proportional only to the field gradient, q about the manganese atom and thus in turn will be proportional to the quadrupole splitting.

$$\sqrt{\Delta H} \propto q \propto Q.S.$$

From the dependance of q on the relative population of the d orbitals it can be shown that if the ligand L is a better σ donor than CO, then q becomes more negative; but if q is a better σ acceptor than CO then q becomes more positive [Chapter 3 (1)]. Thus the line width is proportional to the $|(\sigma-\pi)|$ bonding characteristics of the ligand L.

Thus for the series described in this work the magnitude of the line width and hence the quadrupole splitting (if it could be observed) varies as the $(\sigma-\pi)$ bonding abilities of the ligand, and

increases as C_6F_5 is sucessively replaced by phenyl.

Because there is a linear correlation between the root of the line width and the chemical shift, which are determined by the $(\sigma+\pi)$ and $(\sigma-\pi)$ bonding properties of the ligands respectively, this must mean that σ effects are the predominant feature in determining the line width. If, instead, π effects were the main factor, a line of opposite slope would result, and if σ and π effects were both equally important no correlation at all would be found.

Thus, the amount of σ character in the metal-metal bond for the series $R_3MMn(CO)_5$ (R = Ph, Cl, or C_6F_5 and M = a Group IV metal) increases in the order $Cl_3MMn(CO)_5 > (C_6F_5)_3MMn(CO)_5 > Ph_3MMn(CO)_5$, and thus would be expected to vary in the same sense as the manganese chemical shift since both effects are determined by the σ bonding characteristics of L, as is observed.

This theory is in direct contrast to that of Onaka (225) *et al*, who proposed that the line width is controlled by π effects which increase as the ligand L becomes progressively more electronegative by the substitution of phenyl or methyl with a halogen. Thus it is not correct to say that the line width of the manganese nuclear magnetic absorption is a better reflection of the increasing π effects than the carbonyl stretching force constant k_{co}, since the line width appears to be controlled by the σ donation of L, but k_{co} is mainly dependent on the ability of the ligand to π backbond with the transition metal.

Table 5-6

Manganese Nuclear Magnetic Resonance Data

Chemical Shift in ppm in Acetone Solution upfield from aqueous $KMnO_4$

Compound	$Cl_3MMn(CO)_5$	$(C_6F_5)_3MMn(CO)_5$	$Ph_3MMn(CO)_5$
M = Si	2200 (15)[a]	2290 (6)	2470 (13)
M = Ge	1870 (5)	2140 (9)	2430 (12)
M = Sn	1910 (9)	2260 (11)	2510 (13)
M = Pb	-	-	2350 (14)

Dependence of the Chemical Shift on solvent for $Ph_3SnMn(CO)_5$

Solvent	Chemical Shift (ppm)
Acetone	2510 (13)
Benzene	2410 (13)
Dimethylformamide	ca2505
Tetrahydrofuran	2430 (17)

Table 5-6 cont'd.

Dependance on Line Width to the Chemical Shift

Compound	Chemical Shift (ppm)[b]	Line Width (Hz)[c]
$Ph_3SnMn(CO)_5$	2530 (15)[a]	3000 (300)
$Ph_2(C_6F_5)SnMn(CO)_5$	2470 (16)	2000 (200)
$Ph(C_6F_5)_2SnMn(CO)_5$	2380 (12)	1400 (140)
$(C_6F_5)_3SnMn(CO)_5$	2280 (15)	600 (60)
$Ph_2ClSnMn(CO)_5$	2424 (5)	medium
$PhCl_2SnMn(CO)_5$	2228 (5)	sharp
$Cl_3SnMn(CO)_5$	1967 (5)	very sharp
$Cl(C_6F_5)_2SnMn(CO)_5$	2200 (5)	sharp
$Cl_2C_6F_5SnMn(CO)_5$	2100 (5)	sharp

a) figures in parentheses represent standard deviations
b) THF solvent
c) relative line widths at half height

CHAPTER 6

CONCLUSIONS

The ultimate aim of much of the spectroscopic work on the Group IVB-transition metal bond has been to determine the magnitude of the π contribution in that bond. In inorganic chemistry, in general, the importance of π-bonding has been rather overemphasised and the tendency has been to invoke the π bonding when no other more simple description is apparent. Although the majority of spectroscopic techniques measure a composite σ and π effect, many may be either relatively insensitive to π bonding, while in other cases the measured physical parameter may be only sensitive to a change in σ bonding. Alternatively, in a number of systems which contain a genuine π bond, a small change in π bonding may produce a very substantial change in the σ bonding network, and thus make the effect from π bonding harder to discern.

Although much of the earlier work indicated that there could be a substantial degree of π bonding in the Group IV-transition metal bond, it is now generally accepted on the basis of a wide range of spectroscopic studies, that the metal-metal bond is best considered as a single, non polar, highly polarisable σ bond. There is little evidence for any great degree of π bonding, in spite of the fact that a large degree of π bonding may be inferred from infrared

studies on certain derivatives (218 - 220, 224). The use of semi-empirical approaches, such as the calculation of carbonyl stretching force constants (212, 223) has been criticised (243, 244), and it has been suggested (241) that until the usefulness of such calculations has been conclusively established the carbonyl stretching frequencies themselves are a better guide to the variation in the electronic environment of the metal-metal bond. However, the relative importance of the σ and π bonding contributions in the metal-metal bond cannot be deduced from such data, since the carbonyl stretching frequencies are a measure of the (σ-π) effect in the C-O bond, and need not be directly related to changes in the metal-metal bond itself. It is for this reason that no detailed discussion of the variation in the carbonyl stretching frequencies was attempted in this work. Even the most sophisticated vibrational spectroscopic studies (206, 226, 227) involving a full normal coordinate analysis of the entire molecule seem to contradict the conclusions about the nature and strength of the metal-metal bond reached from other sources. This suggests that either the metal-metal stretching force constant is not a true measure of the strength of that bond, or that other factors are controlling the chemical reactivity and the other spectroscopic properties.

In some cases, composite (σ-π) effects can influence other spectroscopic parameters e.g. the chemical shift of the cyclopentadienyl ring protons in cyclopentadienyl carbonyl derivatives. Again however, factors other than the σ and π contributions are important in determining the magnitude of the chemical shifts. In these compounds,

both the carbonyl stretching frequency and the cyclopentadienyl chemical shifts are related to the variation in electron density about the iron atom, and are substantially in agreement with the interpretation of the iron Mossbauer center shifts. The variation in centre shift is however very small, and is only sensitive to changes in s electron density about the iron atom,and not to either p or d electron density which may be more important in determining the carbonyl stretching frequency or the shift of the cyclopentadienyl ring protons.

Spectroscopic techniques that examine the electronic environment of the metals themselves such as Mossbauer or Nuclear Quadrupole Resonance spectroscopy should be a better indicator of any π bonding between the metals, but even those techniques can only be used where substantial changes in the nature of the metal-metal bond are to be expected as the substituents on the metals change.

For the tris alkyl and tris aryl Group IVB derivatives the invarient nature of the carbonyl stretching frequencies, (48) the ^{57}Fe Mossbauer parometers, the ^{13}C N.M.R. chemical shifts (242), or the ^{57}Co N.Q.R. frequencies (238) to a change in the Group IVB metal, suggest that the electronic environment of the metal-metal bond remains essentially constant, although these derivatives may have a greater σ bond order than the trihalo derivatives.

The Mossbauer studies in this work show that, at least in the case of a tin-transition metal bond, the results can be adequately explained in terms of a σ bond between the two metals. If π bonding in the metal-metal bond was important, and the π electrons were

donated from manganese to tin, then two effects would result: namely, (1) the better π acceptor properties of Cl_3Sn relative to Me_3Sn would decrease the C.S. in the trichlorotin derivative relative to that in the trimethyl tin derivative and (2), the substitution of a carbonyl by a weaker π acceptor ligand such as a phosphine, would decrease the C.S. at the tin in the substituted compound relative to that in the parent derivative. This argument does depend upon the assumption that the π electrons are donated from the transition metal to the tin, and not from the tin to the transition metal. If the latter were the case then the centre shift would decrease in both of the above cases.

However, the direction of π electron flow must be from the manganese to the tin, since the former has filled 3d orbitals of the appropriate symmetry to donate into the empty 5d orbitals on the tin. Conversely, the tin atom has all its 5s and 5p electrons involved in the σ bonding network to its neighbouring groups and thus has no electron density available for donation to manganese. Because a positive increase in the centre shift is observed in both cases (1) and (2), this must be taken as strong evidence against any large degree of π bonding in the metal-metal bond, although it must be remembered that the sensitivity of the centre shift to π effects may not be great, since the centre shift is far more sensitive to changes in s electron density than to changes in either p or d electron density.

Further evidence for the substantial σ nature of the metal-metal bond is obtained from the ^{55}Mn N.M.R. results in this thesis.

Although the factors that affect the chemical shift are not clearly established, the observation that both the chemical shift and the relative line width for the manganese resonance can be correlated with the σ bonding properties of the ligands, must be strong evidence in favour of a σ bond between the two metals. However, this correlation does not prove that these parameters are sensitive only to σ effects.

From the mass spectral studies on some silicon-cobalt tetracarbonyl derivatives it was concluded that there was some evidence for π bonding in the silicon-cobalt bonds. This observation is not in agreement with the N.Q.R. studies (238), which show little evidence for π bonding between these two particular metals, although there may be some evidence for π bonding in the germanium and tin analogues (239, 240). An alternative explanation of the high Si-Co bond energies and short Si-Co bond distances is that the organosilicon species exerts a strong σ effect which increases as the ligands bonding to silicon become more electronegative. This is supported by some molecular orbital calculations which show only a small amount of π bonding in the metal-metal bond (211). In addition, the displacement of the equatorial carbonyl groups from the plane normal to the Si-CO axis and towards the silicon atom need not be a result of any interaction between the carbonyl and the organo silicon group, but simply a result of a steric hinderance due to the short silicon-transition metal bond length (211).

The use of mass spectral data to gain information about the nature of the metal-metal bond must be used with extreme caution,

since although this technique can give meaningful data on the course of high temperature reactions, the heats of formation of various radical species, and an indication of certain specific bond strengths, it is not a suitable technique for systems containing a Group IVB-transition metal bond. In a series of structurally related compounds the variation in the metal-metal bond strength is likely to be smaller than the error in the measurement, and this error is further increased by the uncertainty in the value of the ionisation potential or heat of formation for many of these species. Even detailed analyses of the fragmentation patterns generally do not support the conclusions reached about the strength of the metal-metal bond obtained from other spectroscopic or chemical evidence, although in certain cases a rather remarkable and certainly fortuitous relationship between the two can be found. This is particularly obvious from the mass spectral studies in this work, since although depending upon the nature of the metals, and the number of fluoro-carbon groups several quite distinctive fragmentation patterns can be observed, few of these bear any relationship to the known or expected variation in the metal-metal or metal-carbon bond strength obtained from other sources. Even the identification of organometallic species via mass spectrometry must be treated with caution, for it is known that for some compounds, and particularly for those containing a halogen atom,the observation of an appropriate molecular ion does not conclusively establish the presence of that species in the compound under investigation. This is because redistributions between two or more species or the decomposition or

rearrangement of a single species in the ion source is known to occur (182).

As mentioned in the introduction in this thesis, the use of crystallographic data to infer the relative amount of π character in a metal-metal bond, based upon bond length data must be used with caution since the covalent radii for many metals are not known with certainty, and could conceivably change depending upon the total electronic environment of the metal in a particular compound. Thus the shortness of the Si-Co bond in the compounds $R_3SiCo(CO)_4$ (R = H, Cl or F) (211) could be either a measure of the error in the covalent radii of silicon, or alternatively a manifestation of the strong σ effect of the R_3Si group. A similar shortening of the Sn-Fe bond is also observed in the series $Ph_{3-n}Cl_nSnFe(CO)_2cp$ (135 - 138) as n becomes larger and since on the basis of their Mossbauer spectra, the influence of π bonding in the Sn-Fe bond can be considered to be negligible, this shortening can be attributed to an σ effect which increases the s character of the Sn-Fe bond. It is also true that not all distances that should be an indicator of π bonding are necessarily shortened, since although the Sn-Mn bond in $Ph_3SnMn(CO)_4PPh_3$ (248) is shorter than that in the unsubstituted derivative, a similar shortening is not observed in the Sn-Fe bond between $Me_3SnFe(CO)cpP(Ph)_2\overline{C = CP(Ph)_2(CF_2)_2CF}$ (247) and $Ph_3SnFe(CO)_2cp$ (135). It has been established that the substitution of Me for Ph has no effect upon the Sn-Mn bond length in $Ph_3SnMn(CO)_5$, and thus the constant value for the Sn-Fe bond length in the above compounds is presumably not a consequence of the different groups

bonded to tin. In addition, the Ru-Sn bond length in $[Me_3Sn(CO)_3RuSnMe_2]_2$ trans to the CO group is significantly shortened with respect to the other two Ru-Sn bond lengths even though it is trans to the better π acceptor (246). This is the reverse of what is to be expected on a simple empirical basis, especially when one considers that metal-metal π bonding is supposed to be enhanced with a second or third row transition metal.

Although a large mass of spectroscopic data is available on many different types of Group IVB-transition metal bonds, the general level of interpretation has not been very high.

This perhaps has been due to the fact that although the application of several complementary techniques to a series of structurally related molecules is clearly desirable, this with a few exceptions has not been previously carried out. This thesis has attempted to carry out such a study, but although the series of compounds under study and the spectroscopic techniques used were chosen with care, only a limited amount of information was obtained regarding the nature of the metal-metal bond. This may be due to the fact that the spectroscopic techniques employed in this thesis are essentially independant of each other, such that the conclusions reached by one study are not necessarily consistent with the conclusions reached by the others.

Although the electronic environment of the metal-metal bond appears to be more complex than at first thought, it would appear that in the absence of a radically new spectroscopic technique, e.g. one that directly measures π bonding, the metal-metal bond is best

considered as a σ bond between the two metals.

CHAPTER 7

EXPERIMENTAL

General

All preparative reactions were carried out under nitrogen, but the workup of the solutions and final purifications by recrystallisation were performed in air. Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected.

All samples for mass spectral analysis were sublimed at least once onto an air or water cooled probe at pressures of less than 10^{-2} mm of mercury and temperatures at, or a little below the melting point of the sample.

Sealed tube reactions were carried out in thick walled Carius tubes of sufficient size that the pressure inside the tube was unlikely to exceed five atmospheres at any given time.

Ultraviolet irradiations were carried out in an all quartz apparatus using a 450 watt Hanovia mercury arc lamp, placed as close to the quartz reaction vessel as possible. A slow stream of nitrogen was passed through the solution, and the tube was cooled externally by a stream of air such that the temperature of the solution during the irradiation was maintained at about 50°.

High resolution infrared spectra of the carbonyl absorptions were run on a Beckmann IR-7 spectrometer using the 1601.8 cm^{-1} band of polystyrene as a reference. The samples were run as solutions

in cyclohexane in a matched pair of KBr cells. Less soluble compounds were run in chloroform. The accuracy of the measurements is believed to be ±2 cm^{-1} for cyclohexane solutions and ±4 cm^{-1} for the samples run in chloroform.

Raman spectra of colourless compounds were obtained using a Cary Model 82 laser spectrometer equipped with a triple monochromater and operating on the 5145 Å exciting line of the argon source. Coloured samples were run on a Spex model 1400 double monochromater operating on the 6328 Å line of the helium neon laser. The accuracy of the measurement in both cases was ±2 cm^{-1}. Polarisation studies were carried out in methylene chloride solutions.

Nuclear magnetic resonance data were obtained using the Varian T60 or Varian HA100 spectrometer. Proton resonance spectra were obtained in a variety of solvents using tetramethylsilane as the internal reference.

Mass spectra were obtained on an Associated Electrical Industries MS-12 medium resolution instrument operating at an ionisation voltage of 70 e.v. and at a resolution power of 1000. Samples were introduced directly into the source chamber by means of a heated direct lock insertion probe, and where possible, thermal decomposition was minimised by keeping the temperature of the ion source and probe at, or a little below the melting point of the sample. The intensities of the peaks starting at m/e of 50 were measured using a variable scale ruler (Nuclear Magnetic Resonance Specialties Inc), and adjusted such that the peaks could be read directly as a percentage of the largest (base peak) which was given an arbitary

figure of 100. The intensities of all polyisotopic ions were compared with the theoretical pattern for a given ion and if necessary, possible overlapping species deconvoluted using a computer program developed for this purpose (44). Metastable transitions were also elucidated using a computer program and where several possibilities were mathematically possible, the one or ones that best fitted the expected or previously observed transition were chosen.(44) For the polyisotopic elements, the value of m* calc. refers to the most abundant isotope (i.e. Si^{28}, Ge^{74}, $Sn^{120}$and Fe^{56}).

Appearance potentials were measured on a Bendix Model 12 Time-of-Flight instrument fitted with a Model 14-107 ion source. The samples were introduced via a direct lock insertion probe and the appearance potential was measured using the semi-automatic method of Lloyd and Stafford (249). The ionisation efficiency curves thus obtained were then analysed by a computer program (44) based upon Warren's extrapolated voltage difference method. This program has the advantage that besides eliminating the tedious manual treatment of results, it also give a more reliable assessment of the possible errors.

Mossbauer spectra were obtained with the usual experimental apparatus using an Austin Science Associates linear velocity drive spectrometer. The number of counts was collected via a Nuclear Data multichannel analyser operating on 512 channels over a 5 mm/sec velocity sweep, and in such a manner as to give two mirror images of the spectra.

Iron spectra were obtained using a 50 mc ^{51}Co source set in a

palladium matrix, while the tin spectra were run using a 5 mc $Ba^{119m}SnO_3$ source and cooling the sample to 80°K with liquid nitrogen. The experimental data were retrieved on paper tape and analysed by the computer program developed by Dr. A.J. Stone of the University of Cambridge. The constraint facility of this program allows the resolution of very small and visually unresolved quadrupole splittings. Some examples of the computer plotter output of some representative spectra are given in Figure 7-1.

Manganese 55 nuclear magnetic resonance spectra were obtained on a Varian 4200B Wide line N.M.R. spectrameter using a Varian 3400 nine inch magnet which had a field homogencity of better than 60 milligams over a distance of 15 mm, which is the outside diameter of the sample tubes used. The magnetic field was swept by a Fieldial MkII sweep unit and for ^{55}Mn operated at 14.81 MHz at 14.1 Kgauss. Audiofrequency side bands were added by a Hewlett Packard 241 oscillator and monitored on a Hewlett Packard 522B electronic counter. The signals were recorded as a derivative of their dispersion mode on a varian G-10 strip-chart recorder.

After both the reference and compound signal had been measured, the field sweep reversed direction and the values quoted are an average of at least four sets of signals.

Microanalyses were carred out either by the A.B. Gygli Microanalytical Laboratory of Toronto, Chemalytics Inc. of Arizona, or by the Swarzkopf Microanalytical Laboratory of New York.

Sources of Materials

Pentafluorobenzene and cyclopentadienyldicarbonyliron dimer

The ^{119}Sn Mossbauer Spectra of $Ph_2(C_6F_5)SnMn(CO)_5$

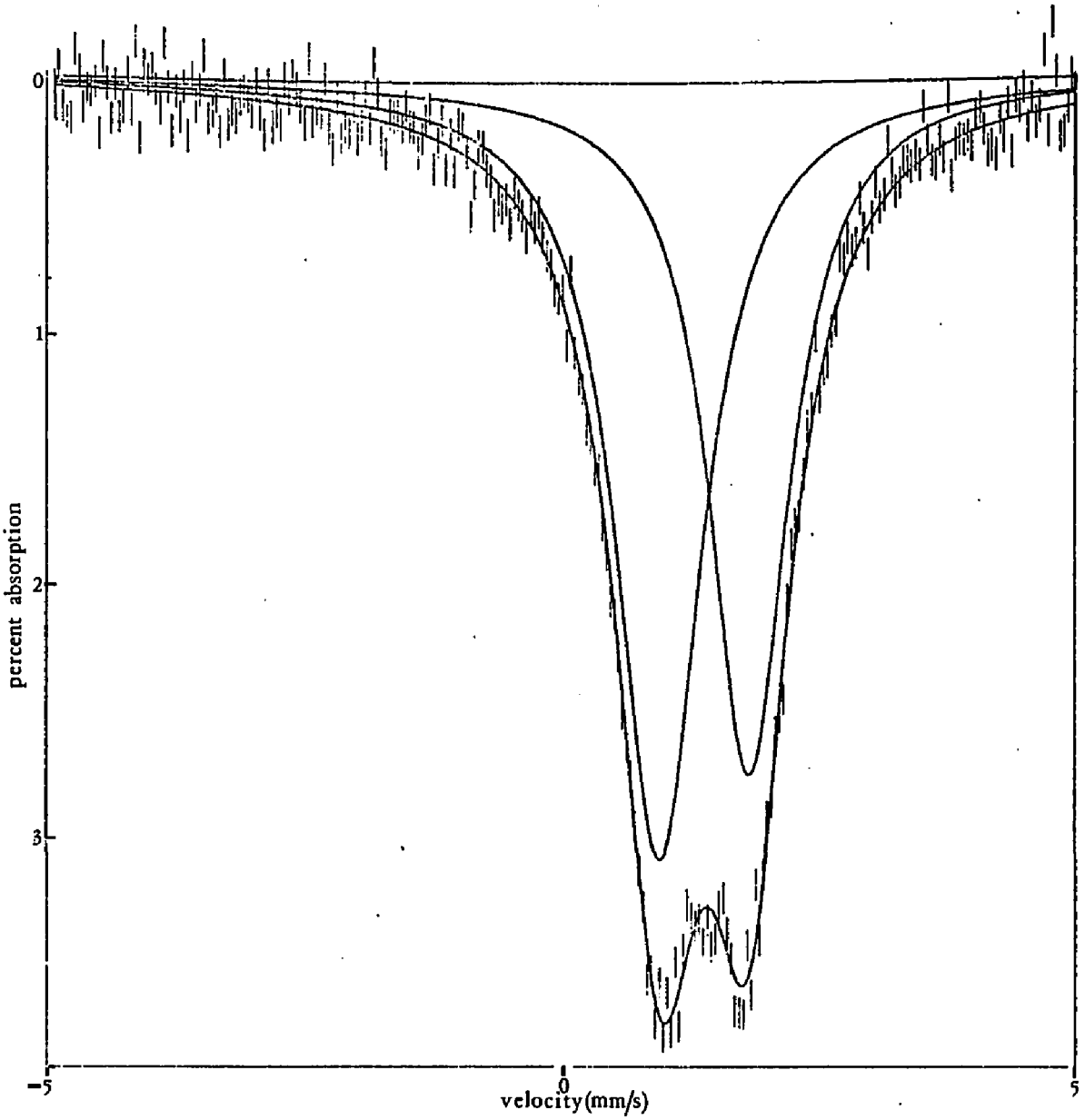


Figure 7-1 (a)

The ^{119}Sn Mossbauer Spectra of $PhCl_2SnFe(CO)_2cp$

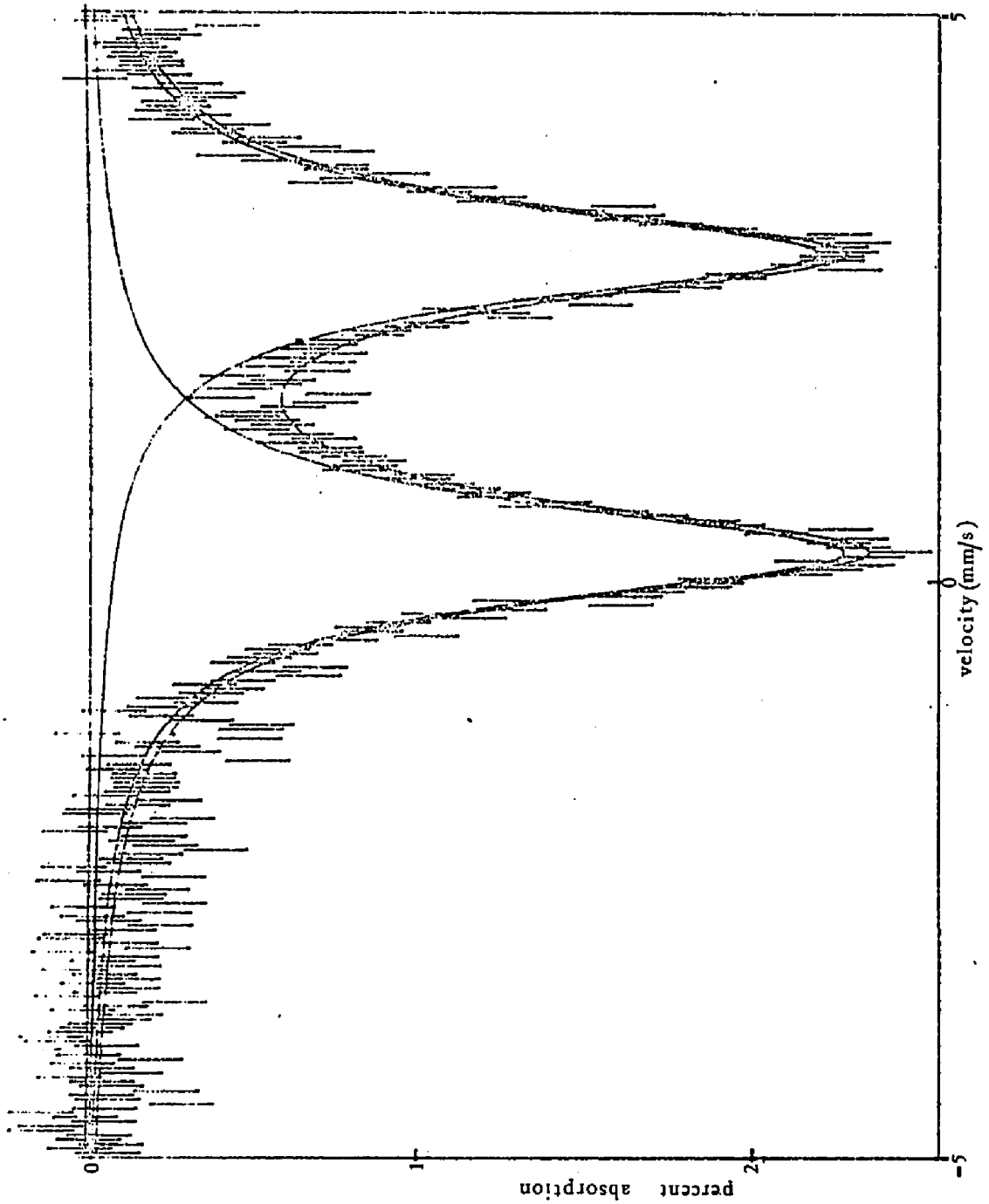


Figure 7-1 (b)

The ^{119}Sn Mossbauer Spectra of $Ph_3SnFe(CO)_2cp$

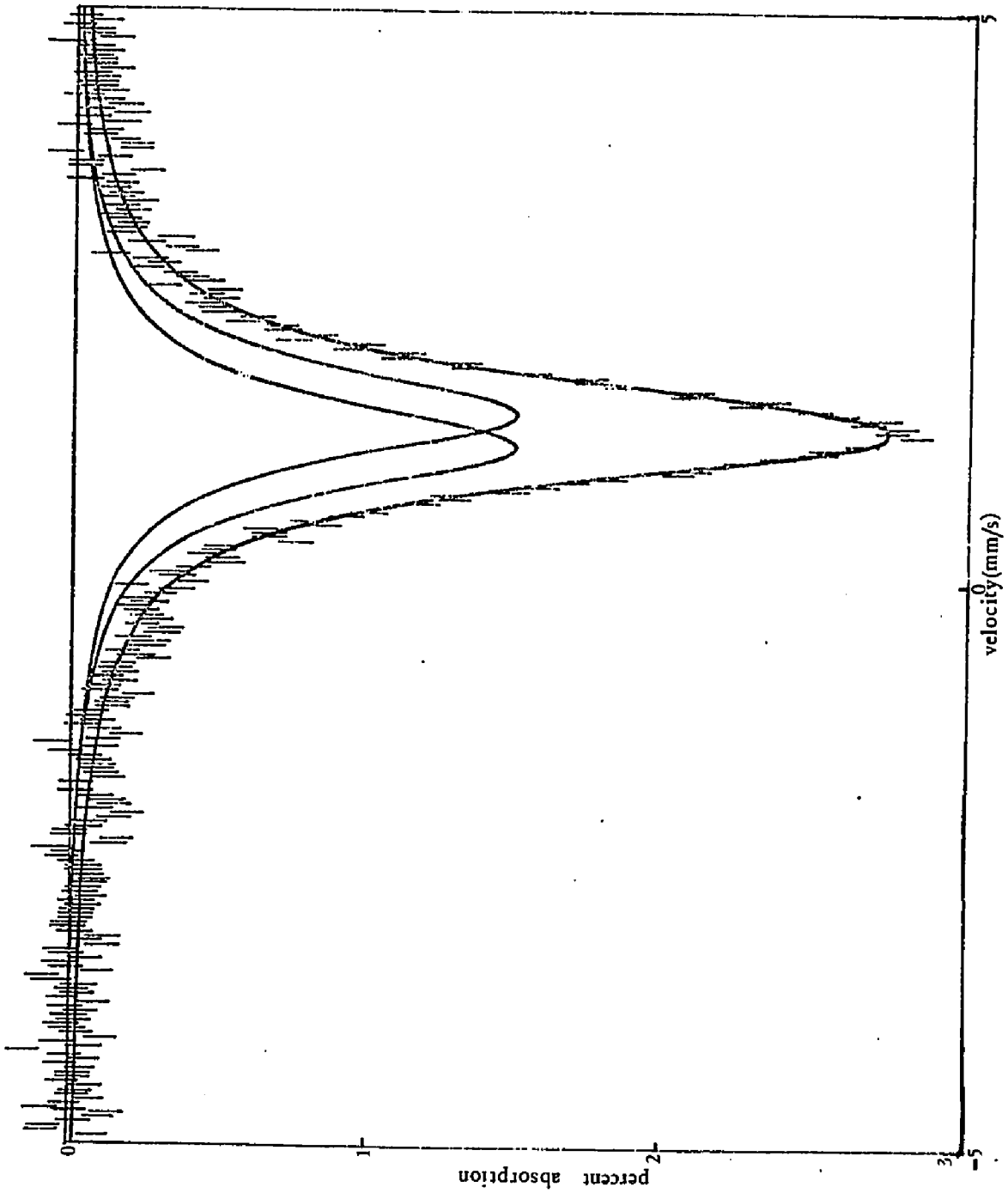


Figure 7-1 (c)

The ^{57}Fe Mossbauer Spectra of $Ph_2ClSnFe(CO)_2cp$

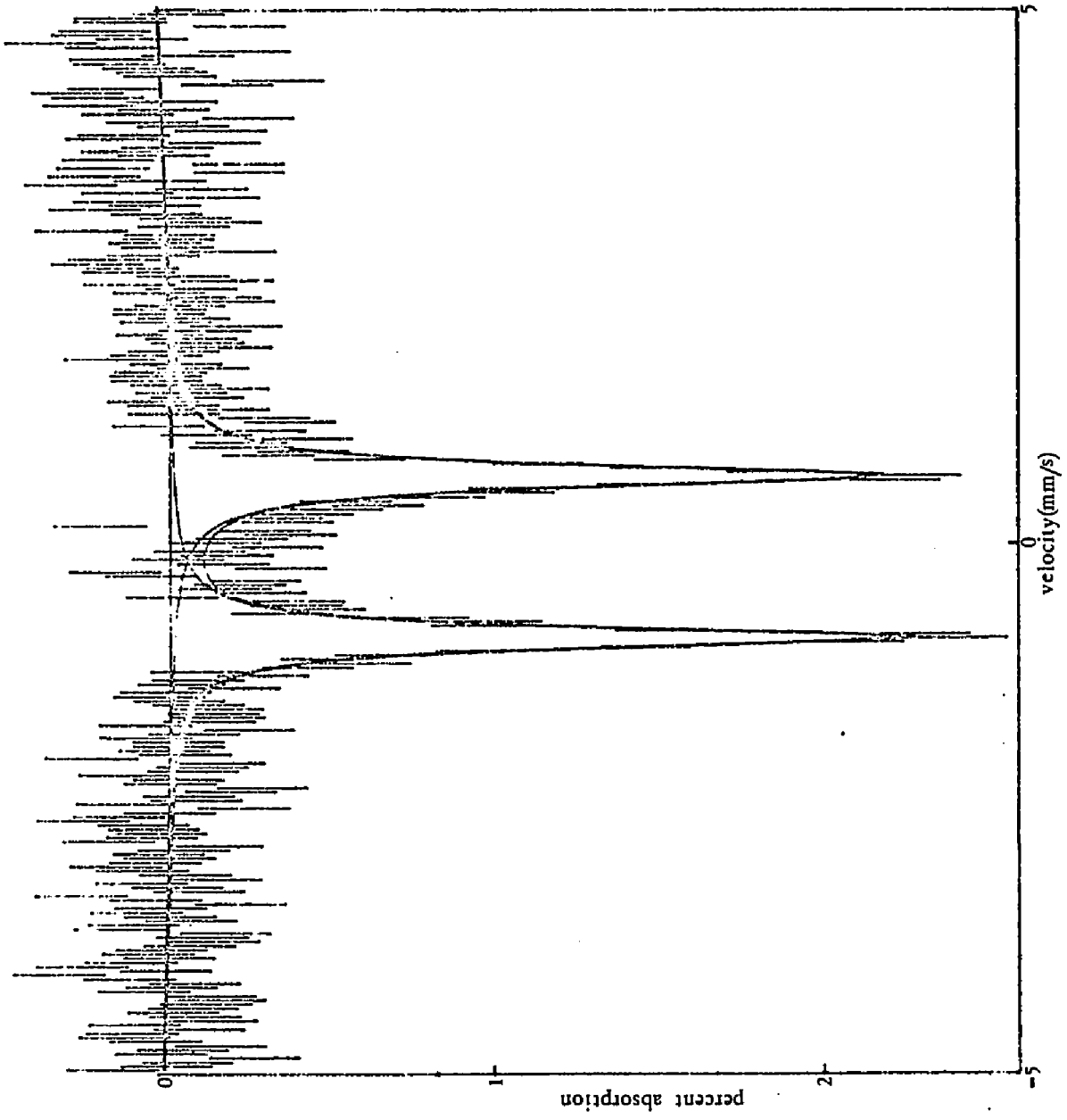


Figure 7-1 (d)

were obtained from the Pierce and Pressure Chemical Companies respectively. Methylcyclopentadienyltricarbonylmanganese was obtained from the Ethyl Corporation, while all the other organometallic compounds used in this work were obtained from Alfa Inorganics Inc. (Ventron).

Tetrahydroforan was dried by distillation under nitrogen over a sodium or potassium benzophenone ketal immediately before use, all the other solvents being used as supplied.

a) Preparation of the Starting Materials

Dimanganesedecacarbonyl was prepared by the method of King (250), from sodium dispersed in boiling diglyme, carbon monoxide and methylcyclopentadienyl manganese tricarbonyl. After a reaction time of 12 to 16 hours the excess sodium was destroyed by the addition of propanol followed by phosphoric acid and the product extracted from the resulting mixture by steam distillation. Apparently the yield is very much improved (251) if the sodium is dispersed into a very fine form by the use of a nichrome wire stirrer, and the apparatus pressurised to 1½ to 2 atmospheres of CO over a 24 hour period. Under atmospheric conditions, the yields of $Mn_2(CO)_{10}$ was about 15% based upon the weight of π-$MeC_5H_4Mn(CO)_3$ used.

Phenyldichlorosilane and diphenylchlorosilane were made by the method of Emelcus and Robinson (252) from trichlorosilane and phenylmagnesium bromide. It was found that the yields were improved if slightly less than the stoecheometric amount of an ether solution of phenylmagnesium bromide was added to a vigorously stirred solution of trichlorosilane in either at -78°. After letting the

flask warm to room temperature, the reaction mixture was refluxed for 12 hours, filtered, and the ether removed under vacuum. The resulting orange oil was fractionally distilled under nitrogen at reduced pressure to give either phenyldichlorosilane (35%; b.pt. 66-68° at 18 mm of mercury) or diphenylchlorosilane (39%; b.pt. 84-86° at less than 1 mm of mercury). The purity of each sample was checked by N.M.R. and or by analysis

$Ph_2Si(Cl)H$ N.M.R.: Ratio of phenyl protons to hydride 10:1 Γ_{SiH} 4.27 in CCl_4. Analysis: Calcd. for $C_{12}H_{11}SiCl$: C, 40.67; H, 3.39; Cl, 40.11 Found: C, 40.12; H, 3.41; Cl, 39.91. $PhSi(Cl)_2H$ N.M.R. Ratio of phenyl protons to hydride 5:1 Γ_{SiH} 4.07 in CCl_4

Phenylbis(pentafluorophenyl)silane and diphenyl(pentafluorophenyl)silane were prepared by the method of Gilman et al (93) by the reaction of an excess of pentafluorophenyllithium upon the corresponding phenylchlorosilane at -78°.

These silanes were not subjected to further purification by vacuum distillation, but the N.M.R. of the crude product showed that the desired compound had been formed, although it was often slightly contaminated by a small amount of impurity thought to be the SiOH species resulting from hydrolysis.

$Ph_2(C_6F_5)SiH$ N.M.R. CCl /rms Ratio of phenyl protons to hydride proton 10:1 Γ_{SiH} 4.27 apparent H-ortho fluorine coupling constant 4.5 Hz

ν_{SiH} 2165 cm^{-1}

$Ph(C_6F_5)SiH$ N.M.R. CCL /rms Ratio of phenyl protons to hydride proton 5:1 Γ_{SiH} 4.23 apparent H-ortho fluorine coupling constant 4.5 Hz

ν_{SiH} 2205 cm^{-1}

Tris(pentafluorophenyl)silane was made by the literature method (71, 253) using THF in place of ether. This gave a 90% yield of $(C_6F_5)_3SiH$ (m. pt. 132 - 134°; lit. 133 - 135°), which was further purified by vacuum sublimation directly before use.

Cyclopentadienyldicarbonyliron iodide was prepared by the literature method by the cleavage of the iron-iron bond in $[Fe(CO)_2cp]_2$ with iodine in refluxing carbon tetrachloride (254). The triphenyl phosphite derivative was made by refluxing $IFe(CO)_2cp$ (3.04 g, 10 m. moles) with triphenyl phosphite (3.8 g, 12.6 m. moles) in benzene for four hours. Filtration of the solution and removal of the solvent gave cyclopentadienylcarbonyl(triphenylphosphite)iron iodide (3.6 g, 6.2 m. moles, 62%) m. pt. 135 - 137° (decomposes)
Analysis calcd for $C_{24}H_{20}O_4PFeI$: C, 49.10; H, 3.41; I, 21.66;
Found: C, 49.67; H, 3.38; I, 21.89

b) Preparation of the Metal-Metal bonded Compounds

1) By the Use of the Sodium Salt of the Metal Carbonyl Anion and the Appropriate Metal Halide in THF

The triphenylgermanium, tin and lead derivatives of pentacarbonylmanganese (48, 23) and cyclopentadienyldicarbonyliron (49, 23, 50, 256) were made according to the literature methods and their purity checked by their melting point, infrared, and proton N.M.R. spectra. The phenylhaloderivatives of germanium and tin were made by similar methods to that of Graham (52) and Newlands (51). The relevant details are summarised in Table 7-1 and a typical reaction is described below.

The Preparation of

Phenyldichlorogermaniumcyclopentadienyldicarbonyliron

A solution of cyclopentadienyldicarbonyliron dimer (2.66 g, 7.5 m. moles) in dry THF (150 mls) was reduced for two hours by sodium amalgam (150 g) containing approximately 1% of sodium under vigourous stirring. The amalgam was then removed via the stopcock attached to the bottom of the flask and the resulting solution of sodio iron cyclopentadienyl dicarbonyl was added dropwise to a stirred solution of phenylgermanium trichloride (3.84 g, 15 m. moles) in THF (100 mls) at 0°. An instantaneous red colour developed and after the addition was complete, the resulting solution was stirred for twelve hours at room temperature. The solvent was then removed in vacuo to leave a viscous red oil which was then dissolved in the minimum amount of a 1:1 benzene cyclohexane solution, refiltered, and stored in the refrigerator overnight. The orange crystals that formed were shown to be phenylchlorogermanium bis(cyclopentadienyldicarbonyliron) $PhClGe[Fe(CO)_2cp]_2$ (600 mgs). These were recrystallised from benzene to give 570 mgs of pure compound, m. pt. 150° (decomp); N.M.R.: Phenyl to cyclopentadienyl proton ratio 1:2 Γ_{cp} 4.93 in $(CD_3)_2CO$. Analysis cald. for $C_{20}H_{15}O_4ClGeFe_2$ C, 44.55; H, 2.80; Cl, 6.58. Found: C, 44.51; H, 2.87; Cl, 6.46 IR ν(CO) in cyclohexane: 2055(w) 2025(m) 2016(m) 2013(s) 1996(m) 1967(m) 1948(m).

The filtrate was then concentrated and crystallised at -15° to give at first deep red crystals of $ClFe(CO)_2cp$ (256 mgs) identified by analysis (Analysis: Calcd. for $C_7H_5O_2FeCl$; C, 39.54; H, 2.35;

Table 7-1

Reactions of $Mn(CO)_5^-$ or $Fe(CO)_2cp^-$ with Ph_2GeCl_2 and $PhGeCl_3$ in THF

Compound	Colour	% Yield	Analysis: Calculated (Found) Carbon	Hydrogen	Chlorine	m. pt.°	Recrystallisation Solvents
$Ph_2ClGeMn(CO)_5$	white	47	44.51 (45.71)	2.19 (2.25)	7.75 (7.46)	100-102	pentane
$PhCl_2GeMn(CO)_5$	white	39	31.76 (32.37)	1.20 (1.34)	17.07 (16.96)	92-93	pentane
$Ph_2ClGeFe(CO)_2cp$	yellow	42	51.89 (52.12)	3.42 (3.45)	8.07 (8.76)	91-94	cyclohexane
$PhCl_2GeFe(CO)_2cp$	orange yellow	17	39.28 (39.32)	2.52 (2.38)	17.86 (17.68)	101-103	cyclohexane/ benzene

The reaction of Ph_2SnCl_2 and $PhSnCl_3$ with $Fe(CO)_2cp^-$ was repeated in the same manner as that described by Newlands (51). In both cases some $ClFe(CO)_2cp$ was formed as indicated by the deep red colour of the reaction mixture, but the yields of $Ph_2ClSnFe(CO)_2cp$ and $PhCl_2SnFe(CO)_2cp$ did not seem to be affected and were the same as those reported.

Cl, 16.70; Found: C, 39.43; H, 2.47; Cl, 17.10) and then finally orange crystals of a new product appeared. These were recrystallised from a mixture of benzene and pentane to give phenyldichlorogermaniumcyclopentadienyldicarbonyliron (846 mgs, 2.1 m. moles, 17%)

In subsequent preparations of this compound no $ClFe(CO)_2cp$ was isolated since it readily decomposes in solution, although the intense red colour of the solution clearly indicated its presence.

2) By the Reaction of an Excess of Silane or Germane with the Transition Metal Carbonyl Dimer in a Sealed Tube at Temperatures of about 150° for 24 Hours

The triphenylsilicon, trichlorosilicon and tris(pentafluorophenyl) silicon derivatives of pentacarbonylmanganese (48, 69, 71) and cyclopentadienyldicarbonyl iron (69, 71) were made by the literature methods. Except for the preparation of $Cl_3SiMn(CO)_5$, $Cl_3GeMn(CO)_5$, and $Cl_3GeFe(CO)_2cp$ where the yields were essentially quantitative, the yields for the other preparations were quite low (15 to 20%) due to the difficulty of controlling the reaction to prevent charring or the formation of other products.

The relevant experimental details for the other preparations are given in Table 7-2 and a typical reaction is described below.

The Preparation of Diphenylchlorosiliconpentacarbonylmanganese

Dimanganesedecacarbonyl (2.34 g, 6.0 m. moles) was heated with a large excess of diphenylchlorosilane (8.5 g, 19.5 m. moles) in a sealed evacuated Carius tube at 150° for twenty-four hours, whereupon the initial green colour of the solution had changed to a pale yellow,

and a small amount of unidentified white material was precipated. The tube was cooled, and opened by hot spotting a scratch on the glass and the contents extracted with pentane, filtered, and the solvent removed in vacuo to give an oil that was cooled to -78°. The mass of crystals that formed were then rapidly filtered and the filtrate cooled again to crystallize out further portions of the product.

The crude product was then twice sublimed in vacuo to give diphenylchlorosiliconpentacarbonylmanganese (7g, 2.4 m. moles, 24%)

It was evident from IR spectrum of the mother liquor that not all of the product had crystallised out since the compound is apparently very soluble in an excess of silane and the involatility of this particular silane made separation very difficult. In addition if only a slight excess of silane was used a large amount of white involatile solid containing no $Mn(CO)_5$ groups was formed, and little or none of the required product was found. The reaction of $Mn_2(CO)_{10}$ with the phenylpentafluorophenyl silanes was investigated but, again due to the very soluble nature of the phenyl pentafluorophenyl silicon manganese compounds, separation of these from the excess silane proved almost impossible although on the basis of the IR spectrum the reaction had proceeded to give the required product.

The phenylchloro and phenyl pentafluorophenylsilicon derivatives of iron cyclopentadienyl dicarbonyl were however much less soluble in the excess silane, and could be satisfactorily crystallised by the addition of a small amount of pentane at -78°.

Table 7-2

Reactions of $Ph_{3-n}X_nSiH$ (X = Cl, or C_6F_5, n = 1 or 2) and Cl_3GeH with $Mn_2(CO)_{10}$ and $[Fe(CO)_2cp]_2$

Compound	Colour	% Yield	Analysis: Calculated (Found) Carbon	Hydrogen	Chlorine	Fluorine	m.pt.°C	Recrystallisation Solvents
$PhCl_2SiMn(CO)_5$	white	30	35.57(35.30)	1.35(1.43)	19.12(19.20)	--	60-62	sublimed
$Ph_2ClSiMn(CO)_5$	white	24	49.49(49.20)	2.42(2.45)	8.58 (8.49)	--	69-71	sublimed
$Ph_2ClSiFe(CO)_2cp$	pale yellow	32	57.78(57.61)	3.80(3.92)	9.00 (8.72)	--	89-94	cyclohexane followed by
							lit.95-96[a]	sublimation
$PhCl_2SiFe(CO)_2cp$	yellow	40	44.18(43.98)	2.83(2.57)	20.11(18.54)	--	82-83	cyclohexane followed by
					--		lit.81-83	sublimation
$Ph(C_6F_5)_2SiFe(CO)_2cp$	pale yellow	32	48.69(48.81)	1.64(1.67)	--	30.83(30.89)	148-150	cyclohexane
$Ph_2(C_6F_5)SiFe(CO)_2cp$	pale yellow	50	57.03(57.28)	2.85(2.95)	--	18.06(18.30)	139-142	cyclohexane
$Cl_3GeMn(CO)_5$	white	95					166-168[b]	cyclohexane
							lit.167-169	cyclohexane
$Cl_3GeFe(CO)_2cp$	orange	95					139-141	cyclohexane/
							lit.139-140[c]	benzene

a) Reference 57
b) Reference 78
c) Reference 76

3) By the Cleavage of the Phenyltin Bond with Halogen or Hydrogen Halides

The preparations of tribromotin and trichlorotin derivatives of pentacarbonylmanganese (23) and cyclopentadienyldicarbonyliron (102) were accomplished by the reaction of an excess of halogen or hydrogen halide respectively, on solutions of the triphenyltin derivatives in carbon tetrachloride. Phenyldichloro and phenyldibromotinpentacarbonylmanganese (23) were made by the reaction of an excess of hydrogen chloride or the stoichemetric amount of bromine on triphenyltinpentacarbonylmanganese in carbon tetrachloride respectively. The other preparations that were accomplished by the cleavage of the tin carbon bond are summarised in Table 7-3, and a typical reaction is described below.

The Preparation of Phenyldichlorotincyclopentadienyldicarbonyliron

Anhydrous HCl was passed into anhydrous ether (200 mls) for about 10 - 15 minutes and the resulting solution standardised by pipetting 10 mls portions into about 40 mls of water and titrating against standard 0.1M NaOH using phenolphthalien as indicator. The molarity of HCl in ether obtained in this way was between 1.0 and 0.5 molar and was periodically redetermined over several weeks.

To a solution of triphenyltincyclopentadienyldicarbonyliron (2.11 g, 4 m. moles) in benzene (20 mls) was added via a burette a solution of HCl in ether (7.14 mls, 8 m. moles of 1.12 M solution) and as quickly as possible the flask was tightly stoppered. The initially yellow solution turned orange and was left at 0^{o} overnight, after which time the smell of HCl gas had completely disappeared from

the solution. The solvent was removed in vacuo to give an orange oil that rapidly crystallised on the addition of a few mls of benzene followed by pentane until precipitation of the product was complete. This gave yellow crystals of phenyldichlorotincyclopentadicarbonyliron (1.2 g, 2.7 m. moles, 68%).

A solution of chlorine in carbon tetrachloride was standardised by pipetting a 10 ml portion into an excess of solid KI into 40 mls of water and litrating the iodine thus liberated against a standard solution of sodium thiosulphate.

The reaction of this solution with the phenylpentafluoro phenyl tin derivatives of manganese pentacarbonyl was accomplished in the same manner as above but in this case the reaction time was extended to four days. The reaction of 2 moles of chlorine with 1 mole of $Ph_2(C_6F_5)SnMn(CO)_5$ gave a small quantity of a yellow precipitate that was tentatively identified by its I.R spectrum as $[ClMn(CO)_4]_2$ thus indicating that some cleavage of the metal-metal bond had occurred.

The reaction of $Ph_2(C_6F_5)SnMn(CO)_5$, $Ph(C_6F_5)_2SnMn(CO)_5$, $(C_6F_5)_3SnMn(CO)_5$ and $(C_6F_5)_3SnFe(CO)_2cp$ with an excess of HCl gave no new products and the starting materials were simply recovered unchanged and were identified by their respective melting points.

Similarly there was no reaction between $Ph_2(C_6F_5)SnFe(CO)_2cp$ and $Ph(C_6F_5)_3SnFe(CO)_2cp$ and the stoicheometric amount of HCl needed to cleave the phenyltin bond, although an excess of HCl cleaved both the phenyl and pentafluorophenyltin bonds as deduced from the analysis of the products.

Table 7-3

a) Reactions of HX with $Ph_3SnFe(cp)L_2$

Compound	Mole ratio of HX	Product	Colour	m. pt. °C	% Yield	Analysis Calculated (Found) Carbon	Hydrogen	X	Recrystallisation Solvents
L = $(CO)_2$ X = Cl	1:1	$Ph_2ClSnFe(CO)_2cp$	yellow	93-95 (lit.100-101)[a]	55	47.01 (47.77)	3.09 (3.09)	7.32 (7.43)	cyclohexane
	2:1	$PhCl_2SnFe(CO)_2cp$	yellow	116.117 (lit.116-117)[a]	68	35.15 (35.37)	2.25 (2.06)	16.00 (15.71)	benzene/pentane
L = CO X = Br	1:1	$Ph_2BrSnFe(CO)_2cp$	yellow orange	107-110	62	43.07	2.83	15.09	cyclohexane
	2:1	$PhBr_2SnFe(CO)_2cp$	orange	96-98	54	29.31 (29.86)	1.85 (1.65)	30.02 (29.70)	cyclohexane/ pentane
L = CO, PPh_3 X = Cl	1:1	$Ph_2ClSnFe(CO)(cp)PPh_3$	orange	172-175	47	60.18 (59.60)	4.18 (3.99)	4.95 (5.76)	cyclohexane
	2:1	$PhCl_2SnFe(CO)(cp)PPh_3$	orange red	164-168	77	53.22 (53.73)	3.70 (3.94)	10.48 (10.27)	cyclohexane/ benzene
	excess	$Cl_3SnFe(CO)(cp)PPh_3$	maroon	185d. (lit.178-185d)[b]	95				benzene/pentane
L = CO, PEt_3 X = Cl	1:1	$Ph_2ClSnFe(CO)(cp)PEt_3$	orange	141-143d.	30	50.09 (50.78)	5.22 (5.14)	6.17 (6.96)	cyclohexane
	2:1	$PhCl_2SnFe(CO)(cp)PEt_3$	orange red	110-112	54	40.49 (40.67)	4.68 (4.51)	13.28 (12.98)	cyclohexane/ benzene
	excess	$Cl_3SnFe(CO)(cp)PEt_3$	maroon	116-123d.	90	29.25 (29.49)	4.06 (3.92)	21.63 (21.83)	benzene/pentane
L = CO, $P(OPh)_3$ X = Cl	1:1	$Ph_2ClSnFe(CO)(cp)P(OPh)_3$	pale yellow	155-157	56	56.40 (56.68)	3.92 (3.65)	4.64 (5.07)	cyclohexane
	2:1	$PhCl_2SnFe(CO)(cp)P(OPh)_3$	yellow	168-171	58	49.70 (50.51)	3.45 (3.38)	9.79 (10.02)	cyclohexane/ benzene

a) Reference 51
b) Reference 114

Table 7-3 cont'd.

Compound	Mole ratio of HX	Product	Colour	m. pt. °C	% Yield	Analysis Calculated (Found) Carbon	Hydrogen	X	Recrystallisation Solvents
	excess	$Cl_3SnFe(CO)(cp)P(OPh)_3$	orange	205-207d.	88	42.10 (41.53)	2.92 (2.64)	15.57 (15.66)	benzene/pentane
L = $P(OPh)_3$ X = Cl	1:1	$Ph_2ClSnFe(cp)[P(OPh)_3]_2$	yellow	105-108	68	60.63 (62.43)	4.29 (4.72)	3.38 (3.84)	cyclohexane
	2:1	$PhCl_2SnFe(cp)[P(OPh)_3]_2$	orange	160-163	75	55.93 (56.14)	4.01 (3.88)	7.04 (7.62)	cyclohexane/ benzene
	excess	$Cl_3SnFe(cp)[P(OPh)_3]_2$	orange	172-177d.	92	50.93 (52.02)	3.11 (3.67)	11.02 (11.21)	benzene/pentane
L = CO, $P(OEt)_3$ X = Cl	excess	$Cl_3SnFe(CO)(cp)P(OEt)_3$	orange	106-108	c	26.67 (26.87)	3.70 (3.53)	19.70 (19.86)	benzene/pentane

b) Reactions of $Ph_2(C_6F_5)SnMn(CO)_5$ and $Ph(C_6F_5)_2SnMn(CO)_5$ with Chlorine

Compound	Mole ratio of Cl_2	Product	Colour	m. pt. °C	% Yield	Analysis Calculated (Found) Carbon	Hydrogen	Fluorine	Chlorine	Recrystallisation Solvents
$Ph_2(C_6F_5)SnMn(CO)_5$	2:1	$Cl_2(C_6F_5)SnMn(CO)_5$	white	75-77	15	23.92 (24.03)	0.00 (0.00)	17.18 (17.44)	12.87 (14.00)	pentane
$Ph(C_6F_5)_2SnMn(CO)_5$	1:1	$Cl(C_6F_5)_2SnMn(CO)_5$	white	87-90	25	29.79 (29.58)	0.00 (0.00)	27.75 (27.84)	5.03 (4.86)	CCl_4

c) obtained from the reaction of excess HCl upon the product of the irradiation of $Ph_3SnFe(CO)_2cp$ with $P(OEt)_3$. $Ph_3SnFe(CO)(cp)P(OEt)_3$ was not isolated.

4) By the Reaction of Halide Derivatives of Metal-metal Bonds with Pentafluorophenyl Lithium

Tris(pentafluorophenyl)tin, phenyl bis(pentafluorophenyl)tin and diphenylpentafluorophenyltinpentacarbonylmanganese were made as described in the literature (52), except that for the preparation of the phenylpentafluorophenyl tin species the bromide derivative was used in the place of the chloride.

All reactions were carried out in ether as solvent although the preparation of $(C_6F_5)_3SnMn(CO)_5$ and $(C_6F_5)_3SnFe(CO)_2cp$ was equally well accomplished in THF. However, the reaction of $Cl_3SiMn(CO)_5$ with C_6F_5Li in THF gave large quantities of a white infusible hydroscopic material that, from its I.R. spectrum, contained no $Mn(CO)_5$ groups. This was probably similar to the 'polymer' found in the reaction of Ph_3SiCl with C_6F_5Li, and is thought to be formed by the attack on THF by some organo silicon halide species (93). The relevant details for these reactions are given in Table 7-4 and its typical reaction is described below.

The Preparation of

Tris(pentafluorophenyl)germaniumcyclopentadienyldicarbonyliron

In a three necked flask fitted with a mechanical stirrer and pressure equalising dropping funnel and cooled to -78° was added pentafluorobenzene (2.18 g,13 m.moles) in anhydrous ether (60 mls). The whole system was flushed with nitrogen for at least 10 minutes, and then a solution of butyl lithium (13 m. mole, 5.4 mls, 23.1 wt % solution in hexane) was added dropwise and the solution stirred for at least two hours. A solution of trichlorogermaniumdicarbonylcyclopentadienyl

iron (1.43 g, 4 m. moles) in ether (70 mls) was then added dropwise over a 10 minute period, after which time the flask and contents were gradually allowed to reach room temperature. At temperatures of around -15° a fine white precipitate of lithium chloride began forming and when ambient temperature had been reached, complete reaction was ensured by refluxing the mixture on a hot water bath for a further 10 minutes. The yellow solution was then filtered and the ether removed in vacuo to give a yellow viscous oil which was taken up in cyclohexane and filtered again. Crystallisation was affected by the addition of pentane to give yellow platelets of tris(pentafluorophenyl)germaniumcyclopentadienyldicarbonyliron (158 g, 2.12 m. moles, 53%).

The reaction of $PhCl_2SiFe(CO)_2cp$ with C_6F_5Li in ether at -78° was unsuccessful. Even with a very large excess of C_6F_5Li and letting the flask reach room temperature very gradually over a period of several hours, only $PhCl_2SiFe(CO)_2cp$ was isolated in 30% recovery.

The reaction of $PhCl_2GeFe(CO)_2cp$ with C_6F_5Li gave a yellow crystalline product which by analysis showed that partial substitution of chloride by C_6F_5 had occurred. The mass spectra of a carefully recrystallised sample showed peaks due to the molecular ion and the successive loss of two carbonyl groups each having the correct isotope pattern and m/e values corresponding to the compound having the formula $PhCl(C_6F_5)GeFe(CO)_2cp$. The analysis however does not agree with the compound being formulated as such, and it would appear from the analysis and infrared data that the

compound is a mixture of mainly $Ph(C_6F_5)_2GeFe(CO)_2cp$ contaminated by $PhCl_2GeFe(CO)_2cp$, and has undergone extensive rearrangement in the ion source to give the observed mass spectrum.

5) By Disproportionation Reactions

Diphenylbromo and diphenylchlorotinpentacarbonylmanganese were made by the literature methods (23) by the disproportionation of equimolor quantities of triphenyltinpentacarbonylmanganese with the phenyldihalotinpentacarbonylmanganese derivatives in the absence of solvent at 150°.

By an exactly analogous procedure $PhCl_2SnFe(CO)_2cp$ was obtained in 60% yield by heating $Ph_2ClSnFe(CO)_2cp$ (97 mgs, 0.2 m. moles) with $Cl_3SnFe(CO)_2cp$ (81 mgs, 0.2 m. moles) in vacuo for four hours at 150°. The product was recrystallised from a cyclohexane benzene mixture and its identity checked by its melting point and N.M.R. spectrum.

By careful intergration of the N.M.R. spectra of the product obtained from the reaction of 2 moles of HBr with 1 mole of $Ph_3SnFe(CO)_2cp$ it was shown that this contained 25% of $Ph_2BrSnFe(CO)_2cp$ as an impurity. This could be removed by recrystallisation, or more conveniently by heating a 0.50 g sample of the impure product with 0.11 g of $Br_3SnFe(CO)_2cp$ in vacuo at 150° for four hours. Recrystallisation of the product from a benzene cyclohexane mixture gave 0.4 g (66%) of pure $PhBr_2SnFe(CO)_2cp$ (m. pt. 96-98°) that showed only one peak in the cyclopentadienyl region of the N.M.R. spectrum and of equal area to that of the phenyl protons.

The reaction of $Ph_2ClGeMn(CO)_5$ (0.914 g, 2 m. moles) with

Table 7-4

Reactions of $Ph_{3-n}Cl_nMX$ (n = 3 to 1, M = Sn, Ge or Si; and X = $Fe(CO)_2cp$ or $Mn(CO)_5$) with C_6F_5Li

Compound	Colour	% Yield of sublimed product	m.p.t°	Analysis: Calculated (Found) Carbon	Hydrogen	Fluorine	Recrystallisation Solvents
$(C_6F_5)_3SnFe(CO)_2cp$	yellow[b]	69	192-196	37.63(37.86)	0.63(0.65)	35.74(36.09)	cyclohexane/ pentane
$Ph(C_6F_5)_2SnFe(CO)_2cp$	yellow	60	119-121	42.45(42.49)	1.42(1.40)	26.88(26.74)	cyclohexane/ pentane
$Ph_2(C_6F_5)SnFe(CO)_2cp$	yellow	73	111-113	49.47(49.41)	2.47(2.41)	15.68(15.43)	cyclohexane/ pentane
$(C_6F_5)_3GeMn(CO)_5$	white	51	168-171	35.95(35.94)	0.00(0.00)	37.05(36.75)	cyclohexane/ pentane
$Ph(C_6F_5)_2GeMn(CO)_5$	white	61	104-106	40.66(40.80)	0.74(0.86)	27.99(28.41)	pentane
$Ph_2(C_6F_5)GeMn(CO)_5$	white	60	81-83	46.89(46.71)	1.70(1.65)	16.14(15.86)	pentane
$(C_6F_5)_3GeFe(CO)_2cp$	yellow	53	192-194	39.95(40.16)	0.67(0.76)	37.93(37.61)	cyclohexane/ pentane
$(C_6F_5)_3SiMn(CO)_5$	white	33	180-182 lit.180-182[a]				cyclohexane/ pentane
$Ph(C_6F_5)_2SiMn(CO)_5$	white	35	105-106	43.51(42.87)	0.79(0.56)	29.96(30.55)	pentane
$Ph_2(C_6F_5)SiMn(CO)_5$	white	30	84-85	50.55(50.59)	1.84(1.72)	17.46(17.84)	pentane
$(C_6F_5)_3SiFe(CO)_2cp$	yellow	5	185-187 lit. 195[a]				cyclohexane/ pentane

a) Reference 71
b) Not very stable in air at room temperature, but can be stored for many months at 0°C without noticable decomposition.

$Cl_3GeMn(CO)_5$ (0.748 g, 2 m. moles) in a sealed tube at 180° for six hours produced upon extraction and recrystallisation from pentane 1.15 g of a compound that melted at 85 - 87°. This was shown by its analysis and I.R. spectrum to consist of largely $PhCl_2GeMn(CO)_5$ but contaminated by some $Ph_2ClGeMn(CO)_5$ which could not be separated.

There was no reaction between $(C_6F_5)_3SiFe(CO)_2cp$ (500 mgs, 0.71 m. moles) and $Ph_2(C_6F_5)SiFe(CO)_2cp$ (372 mgs, 0.71 m. moles) in a sealed tube at 200° for 200° for 24 hours. Extraction and fractional recrystallisation of the contents of the tube gave only the starting materials identified by their melting point and N.M.R. spectra.

6) Other Preparations

Phenylcyclopentadienyldicarbonyliron was made by the method of King et al (255) via the ultraviolet induced decarbonylation of benzoylcyclopentadienyldicarbonyliron in benzene. $PhCOFe(CO)_2cp$ was made by the literature method from PhCOCl and $Na^+Fe^-(CO)_2cp$ (255). $PhCOFe(CO)_2cp$ (11.5 g, 41 m. moles) was dissolved in benzene (40 mls) and irradiated for five hours in an all quartz apparatus as described earlier. At the start of the irradiation the infrared spectrum of the solution showed characteristic absorptions at 1950 and 2010 cm^{-1} due to the carbonyl groups, and at 1613 cm^{-1} due to the acyl group. The latter band decreased in intensity as the irradiation proceeded and simultaneously new carbonyl bands appeared at 2000 and 1965 cm^{-1}. After the complete disappearance of the band at 1613 cm^{-1} the solution was filtered and the solvent removed in vacuo leaving a dark brown oil, which was then dissolved in pentane refiltered

and crystallised at -20° to give large brown crystals of phenylcyclopentadienyldicarbonyliron (7.6 g, 30,3 m. moles, 74%; m. pt. 33 - 35°, lit. 35°)

The Reaction of Phenylcyclopentadienyldicarbonyliron with Trichlorogermane and Ceasium Trichlorogermanate

$PhFe(CO)_2cp$ (3.81 g, 15 m. moles) in T H F (80 mls) was treated dropwise with trichlorogermane (2.86 g, 16 m. moles) in T H F (40 mls). The initially dark brown solution turned deep red and a slight rise in temperature was noted. After two hours it was filtered and the solvent removed to leave a red oil which upon the addition of cyclohexane solidified to give crystals of trichlorogermaniumcyclopentadienyldicarbonyliron (2.18 g, 50%) identified by its melting point 135 - 137°, (lit 139 - 141°) (76) and N.M.R. spectra. The filtrate was evaporated and shown by N.M.R. to consist mainly of $ClFe(CO)_2cp$. There was no sign of the expected insertion product, $PhGeCl_2Fe(CO)_2cp$.

Ceasium trichlorogermanate was prepared by the method of Poskozin (102) via the reduction of germanium tetrachloride with hypophosphoric acid in the presence of dilute HCl. Upon the addition of a 5% molar excess of ceasium chloride the ceasium trichlorogermante that precipitated from the solution was filtered and dried under vacuum.

An excess of C_5GeCl_3 (3.12 g, 10 m. moles) was added to $PhFe(CO)_2cp$ (1.27 g, 5 m. moles) in T H F (50 mls) and the solution stirred for three hours. The solution was then filtered, and the solvent removed in vacuo to give a red oil which was extremely

unstable and extensively decomposed in air to give an insoluble white precipitate. The red oil was shown by N.M.R. to contain mainly $ClFe(CO)_2cp$ but no other cyclopentadienyldicarbonyliron species were found.

The Preparation of the Substituted Complexes of the Type $Ph_3SnFe(CO)_{2-x}(cp)L_x$ ($x = 1$, $L = PPh_3$, PEt_3, $P(OPh)_3$ and $x = 2$, $L = P(OPh)_3$)

These were made as described, (113, 114) by the ultraviolet irradiation of triphenyltincyclopentadienyldicarbonyliron with the appropriate ligand in benzene solution. The relevant details are given in Table 7-5 and a typical reaction is described below.

The Preparation of Triphenyltincyclopentadienylcarbonyl(triphenylphosphine)iron

Triphenyltincyclopentadienyldicarbonyliron (5.27 g, 10 m. moles), and triphenyl phosphine (2.62 g, 10 m. moles), were dissolved in benzene (40 mls) and irradiated for five hours as previously described. The course of the reaction was monitored by I.R. spectroscopy and terminated when the two strong bands due to the carbonyl stretching vibrations of $Fe(CO)_2cp$ group had vanished completely from the spectra, leaving a single, broader band at 1930 cm^{-1}. The resulting dark brown solution was then filtered and concentrated to a small bulk in vacuo. Crystallisation was affected by the addition of cyclohexane and the orange brown crystals thus obtained were recrystallised from a benzene-methanol mixture to give orange crystals of triphenyltincyclopentadienylcarbonyl(triphenylphosphine)iron (4.6 g, 6.0 m. moles, 60%).

An attempt was made to prepare $Ph_3SnFe(CO)(cp)P(OPh)_3$ by the reaction of triphenyltin sodium, prepared from hexaphenylditin and sodium in liquid ammonia (256), with $IFe(CO)(cp)P(OPh)_3$ in THF. Workup of the solution gave sodium iodide, and a brown oil which could not be crystallised. However, the reaction of excess HCl with this oil gave $Cl_3SnFe(CO)(cp)P(OPh)_3$ is about 30% yield, which was identified by its N.M.R. spectrum and comparison with an authentic sample, and showed that the triphenyltin derivative had in all probability been formed.

Table 7-5

Reactions of $Ph_3SnFe(CO)_2cp$ with PPh_3 PEt_3 or $P(OPh)_3$ under Ultraviolet Irradiation

Compound	Colour	% Yield	m. pt. °C	Reaction Time hrs.	Analysis Calculated (found) Carbon	Hydrogen	Recrystallisation Solvents
$Ph_3SnFe(CO)(cp)PPh_3$	orange	60	187-189	5			benzene/methanol
			lit.192-194[a]				
$Ph_3SnFe(CO)(cp)PEt_3$	orange	79	154-156	5	58.39 (58.62)	5.68 (5.43)	benzene/cyclohexane
$Ph_3SnFe(CO)_2(cp)P(OPh_3)$	pale yellow	62	126-128	5	62.30 (62.95)	4.33 (4.27)	cyclohexane
$Ph_3SnFe(cp)\ P(OPh)_3\ _2$	yellow	43	185-187	10[b]	64.91 (65.11)	4.58 (4.58)	cyclohexane/benzene

a) Reference 113
b) At the end of 10 hrs. there was still some monosubstituted derivative present in the reaction mixture, but could be easily separated from the disubstituted compound by fractional crystallisation

REFERENCES

1. A. Ladenburg, Ann. Suppl., 8, 69, (1869).
2. E. W. Abel, Quart. Rev., 133, (1963).
3. B. J. Bulkin and C. A. Rundell, Coordin. Chem. Rev., 2, 371, (1967).
4. P. Chini, Inorg. Chem. Acta. Rev., 2, 31, (1968).
5. J. Lewis, Pure and Appl. Chem., 10, 11, (1965).
6. R. S. Nyholm, Proc. Chem. Soc., 273, (1961).
7. K. L. Watters and W. M. Risen Jr, Inorg. Chem. Acta. Rev., 3, 129, (1969).
8. N. E. Kolobova, A. B. Antonova and K. N. Anisimov, Russian Chem., Rev., 38, 822, (1969), (English Edn.)
9. M. C. Baird, Progress in Inorganic Chem., 9, 1, (1968). F. A. Cotton editor.
10. N. S. Vyuzankin, G. A. Razuvaev and O. A. Kruglaya, Organometal. Chem. Rev., A., 3, 323 (1968).
11. E. H. Brooks and R. J. Cross, Organometal. Chem. Rev. A, 6, 227,(1970).
12. J. F. Young, Adv. in Inorganic and Radiochemistry, 11, 91, (1968).
13. M. R. Booth, Ph.D. Thesis, University of Western Ontario, (1967).
14. R. E. J. Bichler, Ph.D. Thesis, University of Western Ontario, (1969).
15. B. K. Hunter, Ph.D. Thesis, University of Western Ontario, (1969).
16. T. L. Hauw, Ph.D. Thesis, University of Western Ontario, (1971).
17. N. Kutepov, and H. Kindler,Angew Chem., 72, 802, (1960)
18. C. H. Bamford, G. C. Eastmond, and W. R. Maltman, Trans. Faraday Soc., 60, 1432, (1964).
19. R. D. Cramer, E. L. Jenner, R. V. Lindsey and U. G. Stolberg, J. Am. Chem. Soc., 85, 1961, (1963).

20. G. L. Bond and M. Hellier, Chem. and Industry (London), 35, 1965.

21. M. R. Booth, D. J. Cardin , N. A. D. Carey, H. C. Clark, and B. R. Sreenathan, J. Organometal. Chem., 21, 171, (1970).

22. E. W. Abel and G. V. Hutson, J. Inorg. Nucl. Chem., 30, 2339, (1968).

23. R. D. Gorisch , J. Am. Chem. Soc., 84, 2486, (1962).

24. H. C. Clark, J. D. Cotton and J. H. Tsai, Inorg. Chem., 5, 1582, (1966).

25. H. C. Clark and J. H. Tsai, Inorg. Chem., 5, 1407, (1966)

26. R.C. Edmonson and M. J. Newlands, Chem. Comm., 1219, (1968).

27. R. F. Bryan and A. R. Manning, Chem. Comm., 1220, (1968).

28. R. E. J. Bichler and H. C. Clark, J. Organometal. Chem., 23, 427, (1970).

29. R. E. J. Bichler, M. R. Booth and H. C. Clark, J. Organometal. Chem., 24, 145, (1970).

30. A. D. Beveridge and H. C. Clark, J. Organometal, Chem., 11, 601, (1968).

31. H. C. Clark, J. D. Cotton and J. H. Tsai, Can. J. Chem., 44, 903, (1966).

32. H. C. Clark and B. K. Hunter, J. Organometal. Chem., 31, 227, (1971).

33. L. M. Haines and M. H. B. Stiddard, Adv. in Inorganic and Radiochemistry, 12, 53, (1969).

34. G. M. Bancroft, and R. H. Platt, Adv. in Inorganic and Radiochemistry, 000, (1972).

35. J. Lewis and B. F. G. Johnson, Accounts of Chem. Res., 1, 245, (1968).

36. M. I. Bruce, Adv. in Organometal. Chem., 6, 273, (1968).

37. M. Cais and M. S. Lupin, Adv. in Organometal. Chem., 8, 211, (1970).

38. D. B. Chambers, F. Glockling and J. R. C. Light, Quart. Rev., 22, 317, (1968).

39. J. R. Krause, Ph.D. Thesis, University of Western Ontario, (1971).

40. S. J. Band, I. M. T. Davidson, and S. A. Lambert, J. Chem. Soc. A, 2068, (1968).

41. D. J. Cardin, S. A. Keppie, M. R. Litzow, T. R. Spalding, and M. F. Lappert, J. Chem. Soc. A., 2262, (1971).

42. D. R. Bidinosti, and N. S. MacIntyre, Chem. Comm., 555, (1966) and 1, (1967).

43. G. A. Junk, and H. J. Svec, J. Chem. Soc. A., 2102, (1970).

44. L. L. Coatsworth, Ph.D. Thesis, University of Western Ontario, (1971).

45. F. E. Saalfeld, M. V. McDowell and A. G. MacDairmid, Inorg. Chem., 7, 1665, (1968), and 7, 1465, (1968).

46. D. J. Patmore and W. A. G. Graham, Inorg. Chem., 6, 981, (1967) and 7, 771, (1968).

47. H. R. H. Patil and W. A. G. Graham, Inorg. Chem., 5, 1401, (1966).

48. W. Jetz, P. B. Simmons , J. A. J. Thompson, and W. A. G. Graham, Inorg. Chem., 5, 2217, (1965).

49. D. Seyferth, H. P. Hofmann, R. Burton, and J. F. Helling, Inorg. Chem., 1, 227, (1962).

50. R. E. Dessy, and P. M. Weissman, J. Am. Chem. Soc., 88, 5124, (1966).

51. D. S. Field, and M. J. Newlands, J. Organometal. Chem., 27, 213, (1971).

52. J. A. J. Thompson and W. A. G. Graham , Inorg. Chem., 6, 1875, (1967).

53. R. C. Edmonson, E. Eisner, M. J. Newlands, and L. K. Thompson, J. Organometal. Chem., 35, 119, (1972).

54. T. S. Piper, D. Lemal and G. Wilkinson, Naturwissenschaften, 43, 129, (1956).

55. M. A. Nasta, A. G. MacDairmid and F. E. Saalfeld, J. Am. Chem. Soc., 94, 2449, (1972),

56. M. D. Curtis, Inorg. Chem., 11, 802, (1972).

57. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. V. Shripkin, Izv. Akad. Nauk. S.S.S.R. Ser. Khim., 2364, (1967).

58. B. J. Aylett, and J. M. Campbell, J. Chem. Soc. A., 1910, (1969), and 1916, (1969).

59. A. D. Berry, and A. G. MacDairmid, Inorg. Nucl. Chem. Lett., 5, 601, (1969).

60. M. F. Lappert, and B. M. Kingston, J. C. S. Dalton, 69, (1972).

61. W. R. Knoll, and G. B. McVicker, Chem. Comm., 591, (1971).

62. J. D. Smith, and R. R. Shrieke, J. Organometal. Chem., 31, 446, (1971).

63. J. D. Cotton, S. R. A. Knox, I. Paul, and F. G. A. Stone, J. Chem. Soc. A., 264, (1967).

64. O. Kahn, and M. Bigorgne, J. Organometal. Chem., 10, 137, (1967).

65. W. A. G. Graham, and W. Jetz, Inorg. Chem., 10, 4, (1971).

66. W. A. G. Graham, and A. J. Oliver, Inorg. Chem., 10, 1, (1971).

67. W. A. G. Graham, and R. Kummer, Inorg. Chem., 7, 1208, (1968), and 7, 523, (1968).

68. W. A. G. Graham, and W. Jetz, Inorg. Chem., 10, 1647, (1971).

69. W. A. G. Graham, and W. Jetz, J. Am. Chem. Soc., 89, 2773, (1967).

70. A. J. Chalk, and J. F. Harrod, J. Am. Chem. Soc., 87, 1133, (1965).

71. R. R. Schrieke, and B. O. West, Austr. J. Chem. 22, 43, (1969).

72. Y. L. Baay, and A. G. MacDairmid, Inorg. Nucl. Chem. Lett., 3, 159, (1967).

73. W. A. G. Graham, and W. Jetz, Inorg. Chem., 10, 1159, (1967).

74. D. J. Cardin, S. A. Keppie, and M. F. Lappert, J. Chem. Soc. A. 2594, (1970).

75. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, Izv. Akad. Nauk. S.S.S.R. Ser. Khim., 1319, (1965).

76. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, Izv. Akad. Nauk. S.S.S.R. Ser. Khim., 2246, (1966).

77. R. B. King, Accounts of Chem. Res., 3, 417, (1969).

78. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, Dolk, Akad. Nauk. S.S.S.R., 176, 844, (1967).

79. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, Proc. Acad. Sci. U.S.S.R., 156, 502, (1964).

80. A. N. Nesmegonov, K. N. Anisimov, N. E. Kolobova and M. Ya. Zakhonova, Dalk. Akad. Naak. S.S.S.R., 156, 612, (1964).

81. A. D. Beveridge, and H. C. Clark, unpublished observations

82. J. M. Burlitch, J. A. Chem. Soc. 91, 4562, (1969).

83. The Chemical Society Specialists Peridocial Reports; Fluorocarbon and Related Chemistry, Vo. 1, Edited by R. E. Banks and M. G. Barlow, (1972).

84. L. A. Wall, R. E. Donadio, and W. J. Pummer, J. Am. Chem. Soc., 82, 4846, (1966).

85. M. Fild, O. Glemser, and G. Christoph, Agnew. Chem. Internat. Edn., 3, 801, (1964).

86. D. E. Fenton, A. J. Park, D. Shaw, and A. G. Massey, J. Organometal. Chem., 2, 437, (1964).

87. R. H. Harper, E. J. Soloski, and C. Tamborski, J. Org. Chem., 29, 2385, (1964).

88. R. J. DePasquale, and C. Tamborski, J. Org. Chem. Soc., 3237, (1962).

89. A. E. Jukes, S. S. Dua, and H. Gilman, J. Organometal. Chem., 21, 241, (1970).

90. W. A. Sheppard, J. Am. Chem. Soc., 92, 5419, (1970).

91. A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, And R. J. O'Brien, Chem. Comm., 155, (1971).

92. R. D. Chambers, and T. Chivers, Organometal. Rev., 1, 279, (1966)

93. F. W. G. Fearon, and H. Gilman, J. Organometal. Chem., 10, 409, (1967).

94. D. J. Darensbourg, and M. Y. Darensbourg, Inorg. Chem., 9, 1891, (1970).

95. A. R. Manning, and P. Hackett, J. Organometal. Chem., C 15, (1972).

96. D. J. Patmore, and W. A. G. Graham, Inorg. Chem., 5, 1586, (1966).

97. M. J. Mays, and S. M. Pearson, J. Chem. Soc. A., 136, (1969).

98. F. Bonati, and G. Wilkinson, J. Chem. Soc., 179, (1964).

99. D. J. Patmore, and W. A. G. Graham, Inorg. Chem., 5, 1405, (1966).

100. F. Bonati, S. Lepini, D. Morelli, and R. Ugo, J. Chem. Soc. A., 1052, (1966).

101. N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, J. Chem. Soc. A., 1130, (1966).

102. R. C. Edmonson, and M. J. Newlands, Chem. and Ind. (London), 1888, (1966).

103. P. S. Poskozin, J. Organometal. Chem., 12, 115, (1968).

104. P. S. Poskozin, and A. L. Stone, J. Organometal. Chem., 16, 314, (1969).

105. J. D. Cotton, and R. M. Peachey, Inorg. Nucl. Chem. Lett., 6, 727, (1970).

106. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, Dolk. Akad. Nauk. S.S.S.R., 192, 813, (1970).

107. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandzohko, Izv. Akad. Nauk. S.S.S.R. Ser. Khim, 160, (1966).

108. K. Ogino and T. L. Brown, Inorg. Chem., 10, 517, (1971).

109. A. R. Manning, J. Chem. Soc. A., 1984, (1967).

110. P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, Inorg. Chem., 5, 1177, (1966).

111. R. J. Haines, and A. L. DuPreez, Inorg. Chem., 8, 1459, (1969).

112. J. P. Bibler and A. Wojcicki, Inorg. Chem., 5, 889, (1966).

113. J. F. Bald, and A. G. MacDairmid, J. Organometal. Chem., 22, C 22, (1970).

114. W. R. Cullen, J. R. Sams, and J. A. J. Thompson, Inorg. Chem., 10, 843, (1971).

115. R. B. King, and K. H. Pannell, Inorg. Chem., 7, 1510, (1968).

116. G. M. Bancroft, K. D. Butler, and A. T. Rake, J. Organometal. Chem., 34, 137, (1972).

117. M. G. Clark, A. G. Maddock, and R. H. Platt, J. C. S. Dalton, 281, (1972).

118. G. M. Bancroft, M. J. Mays, and B. E. Prater, J. Chem. Soc. A., 956, (1970).

119. R. V. Parish, and R. H. Platt, J. Chem. Soc. A., 2145, (1969).

120. R. V. Parish, and R. H. Platt, Inorg. Chem. Acta., 4, 65, (1970).

121. G. M. Bancroft, R. E. B. Garrod, and A. G. Maddock, J. Chem. Soc. A., 3165, (1971).

122. D. E. Fenton, and J. J. Zuckerman, J. Am. Chem. Soc., 90, 6226, (1968).

123. R. H. Herber, and Y. Goscinny, Inorg. Chem., 7, 1293, (1968).

124. C. Wynter, and L. Chandler, Bull. Chem. Soc. Japan, 43, 2115, (1970).

125. D. E. Fenton, and J. J. Zuckerman, Inorg. Chem., 8, 1771, (1969).

126. A. N. Karasev, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. N. Anisimov, Teor. i Eksp. Khim., Akad. Nauk. Ukv ., 2, 126, (1966).

127. V. I. Gol'donskii, B. V. Borshagovskii, E. F. Makorov, R. A. Stukan, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, Teor. i Eksp, Khim. Akad Nauk Ukv., 3, 478, (1967).

128. S. Onoka, Y. Sasaki, and H. Sano, Bull. Chem. Soc. Japan, 44, 726, (1971).

129. S. R. A. Bird, J. D. Donaldson, A. F. Lec. Holding, B. J. Senior, and M. J. Tricker, J. Chem. Soc. A., 1616, (1971).

130. S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, J. Chem. Soc. A., 1311, (1971).

131. B. A. Goodman, R. Greatrex, and N. N. Greenwood, J. Chem. Soc. A., 1868, (1971).

132. T. C. Gibb, R. Greatrex, and N. N. Greenwood, J. C. S. Daton, 239, (1972).

133. B. V. Liengme, M. J. Newlands, and J. R. Sams, Inorg. Nucl. Chem. Lett., 7, 1223, (1971).

134. H. P. Weber, and R. F. Bryan, Chem. Comm., 443, (1966).

135. R. F. Bryan, J. Chem. Soc. A., 192, (1967).

136. P. J. Greene, and R. F. Bryan, J. Chem. Soc. A., 1696, (1970).

137. P. J. Greene, and R. F. Bryan, J. Chem. Soc. A., 2261, (1970).

138. G. A. Melson, P. F. Stokely, and R. F. Bryan, J. Chem. Soc. A., 2247, (1970).

139. K. D. Butler, private communication

140. A. G. Maddock, and R. H. Platt, J. Chem. Soc. A., 1191, (1971).

141. G. M. Bancroft, and K. D. Butler, unpublished observations

142. G. M. Bancroft, K. D. Butler, A. T. Rake, and B. Dale, J.C.S. Dalton, in press.

143. R. V. Parish, Progress in Inorganic Chemistry, in press.

144. K. L. Leung and R. H. Herber, Inorg. Chem., 10, 1020, (1971).

145. R. V. Parish, and R. H. Platt, Inorg. Chem. Acta., 4, 589, (1970).

146. T. Chivers, and J. R. Sams, J. Chem. Soc. A., 928, (1970).

147. R. W. J. Wedd, and J. R. Sams, Can. J. Chem., 48, 71, (1970).

148. P. G. Smith, Organometallic Rev., A, 5, 373, (1970).

149. H. Sano, and H. A. Stockler, Trans. Faraday Society., 64, 577, (1968).

150. P. T. Greene, and R. F. Bryan, J. Chem. Soc. (A), 2549, (1971).

151. N. G. Bokii, G. N. Zakharova, and Yu. T. Struchkov, Zhur. Strukt. Khim. (English translation), 11, 828, (1970).

152. B. T. Kilbourne, and H. M. Powell, Chem. and Ind., 1578, (1964).

153. J. E. O'Connor, and E. R. Corey, Inorg. Chem., 6, 968, (1967).

154. B. P. Biryokov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, Chem. Comm., 159, (1968), and 1193, (1968).

155. R. R. Berrett, and B. W. Fitzsimmons, J. Chem. Soc. A., 525, (1967).

156. R. H. Herber, R. B. King, and G. K. Wertheim, Inorg. Chem., 3, 101, (1964).

157. G. M. Bancroft, and E. T. Libbey, unpublished observations.

158. R. H. Herber, and Y. Goscinny, Inorg. Chem., 7, 1293, (1968).

159. S. Pignatoro, and F. P. Lossing, J. Organometal. Chem., 11, 571, (1968), and 10, 531, (1967).

160. H. J. Svec, and G. A. Junk, Inorg. Chem., 7, 1688, (1968).

161. S. M. Schildcrout, G. A. Pressley, and F. E. Stafford, J. Am. Chem. Soc., 89, 1617, (1967).

162. W. A. Chupka, J. Chem. Phys., 30, 191, (1965).

163. A. Cassuto, In "Mass Spectrometry" edited by R. I. Reed, Academic Press Inc., London (1965), p. 283.

164. B. Steiner, C. F. Giese, and M. G. Inghram , J. Chem. Phys., 34, 189, (1961).

165. W. A. Chupka, J. Chem. Phys., 54, 1936, (1971).

166. S. N. Foner, and R. L. Hudson, J. Chem. Phys., 36, 2681, (1962).

167. J. Berkowitz, and W. A. Chupka, J. Chem. Phys., 45, 1287, (1966).

168. K. M. Mackay, S. T. Hosfield, and S. R. Stobart, J. Chem. Soc. A., 2937, (1969).

169. M. F. Lappert, J. B. Pedley, J. Simpson, and T. R. Spalding, J. Organometal. Chem., 29, 195, (1971).

170. R. W. Kiser; In "An Introduction to Mass Spectrometry and its Applications", Prentice Hall, Englewood Cliffs, N. J. U.S.A., (1965).

171. J. W. Warren, Nature., 165, 810, (1950).

172. J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, J. Chem. Soc. A., 1663, (1966).

173. B. F. G. Johnson, J. Lewis, J. M. Wilson, D. J. Thompson, J. Chem. Soc. A., 1445, (1967).

174. B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, J. Chem. Soc. A., 338, (1967).

175. B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, J. Chem. Soc. A. 341, (1967).

176. B. F. G. Johnson, J. Lewis, K. Edgar, I. G. Williams, and J. M. Wilson, J. Chem. Soc. A., 379, (1967).

177. J. M. Smith, K. Mehner, and H. D. Kaesz, J. Am. Chem. Soc., 89, 1759, (1967).

178. G. A. Junk, and H. J. Svec, J. Chem. Soc. A., 2102, (1970).

179. G. A. Junk, F. J. Preston, H. J. Svec, and D. T. Thompson, J. Chem. Soc. A., 3171, (1970).

180. D. B. Chambers, G. E. Coates, F. Glockling, and M. Weston, J. Chem. Soc. A., 1712, (1969).

181. J. M. Miller, Can. J. Chem., 47, (1969).

182. J. M. Miller, J. Chem. Soc. A., 828, (1967).

183. G. F. Lanthier, J. M. Miller, and T. Chivers, J. Chem. Soc. A., 2557, (1971).

184. F. Glockling, J. R. C. Light, and R. G. Stafford, J. Chem. Soc. A., 427, (1970).

185. J. M. Miller, and A. T. Rake, J. Chem. Soc. A., 1881, (1970).

186. G. F. Lanthier, and J. M. Miller, Org. Mass. Spectrom., 6, 89, (1972).

187. J. H. Bowie, and B. Nussey, Org. Mass. Spectrom., 3, 933, (1970).

188. S. C. Cohen, A. G. Massey, G. F. Lanthier, and J. M. Miller, Org. Mass. Spectrom, 6, 373, (1972).

189. A. Carrick, and F. Glockling, J. Chem. Soc. A., 913, (1968).

190. F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, J. Am. Chem. Soc., 2324, (1970).

191. R. B. King, Org. Mass. Spectrom., 2, 657, (1969).

192. M. J. Mays, and R. N. F. Simpson, J. Chem. Soc. A., 1936, (1967).

193. A. K. Bhattacharga, L. D. Smithson, F. L. Hedberg, Org. Mass. Spectrom., 4, 383, (1970).

194. J. D. Hawthorne, M. J. Mays, and R. N. F. Simpson, J. Organometal. Chem., 12, 407, (1968).

195. R. G. Cavell, and R. C. Dobbie, Inorg. Chem., 6, 1450, (1967).

196. R. G. Cavell, and R. C. Dobbie, Inorg. Chem., 7, 690, (1968).

197. J. M. Miller, unpublished results.

198. D. B. Chambers, and F. Glockling, J. Chem. Soc. A., 735, (1968).

199. A. Bos, Chem. Comm., 26, (1972).

200. M. I. Bruce, and M. A. Thomas, Org. Mass. Spectrom., 1, 835, (1968).

201. D. B. Chambers, and F. Glockling, Inorg. Chem. Acta., 1, 150, (1970).

202. A. L. Yergey, and F. W. Lampe, J. Organometal. Chem., 15, 339, (1968).

203. E. C. Tift, Ph.D. Thesis, S.U.N.Y. Syracuse, (1970).

204. D. R. Stevenson, Discuss. Farad. Soc., 10, 35, (1951).

205. J. A. Morrison, Rev. Pure and Appl. Chem., 5, 22, (1955).

206. K. L. Watters, J. N. Brittain, and W. M. Risen Jr., Inorg. Chem., 8, 1374, (1969).

207. A. P. Hagen, and A. G. MacDairmid, Inorg. Nucl. Chem. Lett., 345, (1970).

208. V. G. Weibe, personal communication

209. T. L. Cottrell, In "The Strength of Chemical Bonds", 2nd edition, Butterworths, London, (1958).

210. J. B. Wilford, and F. G. A. Stone, Inorg. Chem., 4, 389, (1965).

211. A. D. Berry, E. R. Carey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, J. Am. Chem. Soc., 92, 1940, (1970), and references therein.

212. F. A. Cotton, and C. S. Kraihanzel, J. Am. Chem. Soc., 84, 4432, (1962).

213. J. Dalton, Inorg. Chem., 11, 915, (1972).

214. M. A. El-Sayed, and H. D. Kaesz, J. Mol. Spectry., 9, 310, (1962).

215. L. E. Orgel, Inorg. Chem., 1, 25, (1962).

216. M. A. El-Sayed, and H. D. Kaesz, Inorg. Chem., 2, 158, (1963).

217. M. Bigorgne, and R. Poilbanc, Bull. Soc. Chim. France, 1301, (1962).

218. J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, J. Chem. Soc. A., 1195, (1968).

219. J. Dalton, I. Paul, and F. G. A. Stone, J. Chem. Soc. A., 1212, (1968).

220. E. W. Abel, J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, J. Chem. Soc. A., 1203, (1968).

221. J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, J. Chem. Soc. A., 1199, (1968).

222. O. Kahn, and M. Bigorgne, Compt. Rend., 263 C, 973, (1966).

223. W. A. G. Graham, Inorg. Chem., 7, 315, (1968).

224. J. Dalton, I. Paul, and F. G. A. Stone, J. Chem. Soc. A., 2744, (1969).

225. S. Onaka, T. Miyomoto, and Y. Sasaki, J. Bull. Soc. Japan, 44, 1851, (1971).

226. K. L. Watters, W. M. Butler, and W. M. Risen Jr., Inorg. Chem., 10, 1970, (1971).

227. R. J. Ziegler, J. M. Burlitch, S. E. Hayes, and W. M. Risen Jr., Inorg. Chem., 11, 702, (1972).

228. S. Onaka, Bull. Chem. Soc. Japan, 44, 2135, (1971).

229. J. M. Burlitch, and A. Ferrari, Inorg. Chem., 9, 563, (1970).

230. C. O. Quicksall, and T. G. Spiro Inorg. Chem., 8, 2363, (1969).

231. H. M. Gager, J. Lewis, and M. J. Ware, Chem. Comm., 46, (1966).

232. D. M. Adams, In "Metal-Ligand and Related Vibrations", Arnold Press, London, (1967).

233. N. A. D. Carey, and H. C. Clark, Inorg. Chem., 7, 44, (1968).

234. R. B. King. Inorg. Chem. Acta., 2, 454, (1968).

235. F. Calderazzo, E. A. C. Lucken, and D. F. Williams, J. Chem. Soc. A., 154, (1967).

236. W. J. Miles, B. B. Garrett, and R. J. Clark, Inorg. Chem., 8, 2817, (1969).

237. R. F. Fenske, and R. L. DeKock, Inorg. Chem., 9, 1053, (1970).

238. T. A. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, Inorg. Chem., 8, 763, (1969).

239. D. D. Spencer, J. L. Kirsch, and T. L. Brown, Inorg. Chem., 9, 237, (1970).

240. J. D. Graybeal S. D. Ing, and M. W. Hall, Inorg. Chem., 9, 678, (1970).

241. K. Edgar, J. Lewis, A. R. Manning and J. R. Miller, J. Chem. Soc. A., 1217, (1968).

242. D. A. Gansow, D. A. Schexnayden , and B. Y. Kimira, J. Am. Chem. Soc., 94, 3406, (1972).

243. F. A. Cotton, Inorg. Chem., 7, 1683, (1968).

244. L. H. Jones, Inorg. Chem., 7, 1681, (1968).

245. D. A. Duddell, P. L. Goggin , R. J. Goodfellow, J. G. Smith, and M. G. Norton, J. Chem. Soc. A., 545, (1970).

246. S. F. Watkins, J. Chem. Soc. A., 1552, (1969).

247. F. W. B. Einstein, and R. Restivo, Inorg. Chem. Acta., 5, 501, (1971).

248. R. F. Bryan, J. Chem. Soc. A., 172, (1967).

249. R. T. Loyd, and F. E. Stafford, In "Mass Spectrometry in Organic Chemistry", chapter 10, Advances in Chemistry Series, A.C.S., Washington, D.C.

250. R. B. King, J. Organometal. Chem., 841, (1968).

251. M. L. H. Green, private communication

252. H. J. Emeléus, and S. R. Robinson, J. Chem. Soc. 1592, (1947).

253. M. F. Lappert, and J. Lynch, Chem. Comm., 750, (1968).

254. Inorganic Synthesis, 7, 110, (1963).

255. R. B. King, and M. B. Bisnette, J. Organometal. Chem., 2, 15, (1964).

256. G. E. Coates, D. Blake, and J. M. Tate, J. Chem. Soc., 618, (1961).

257. R. Ugo, S. Cenini, and F. Bonati, Inorg. Chem. Acta., 1, 415, (1967).

258. J. N. Murrell, and A. B. Nickoloskii, J. Chem. Soc. A., 1363, (1970).